BIOREFINERIES - THE DEPARTMENT OF ENERGY VIEWPOINT

Douglas Kaempf

U.S. Department of Energy, Office of the Biomass Program, EE-22
1000 Independence Ave., S.W., Washington, DC 20585
(202) 586-5264: douglas.kaempf@ee.doe.gov

Abstract

The biorefinery concept allows for maximum return on our limited biomass resources for production of fuels, chemicals and power to reduce our dependence on foreign petroleum imports. This presentation will present the research and development program of the Office of the Biomass Program for technologies needed to bring the biorefinery industry to reality.

CHEMICAL BUILDING BLOCKS FOR THE BIOREFINERY

Todd A. Werpy

Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99352

The petrochemical industry has been established on the concept of producing both fuels and chemicals at a single integrated facility. This model allows the economy of scale from the production of fuels as well as the creation of higher value chemical constituents. This same model can be applied to a biorefinery in which fuels, chemicals and heat and power are produced in a single facility. One of the big challenges is deciding which chemicals will be integrated into that facility and what product options exist. This talk will focus on a specific example of using a 4 carbon building block (succinic acid) as a model for producing a variety of chemicals within a biorefinery.

FAST PYROLYSIS BASED BIO-REFINERIES

Tony Bridgwater

Aston University Bio-Energy Research Group, Birmingham B4 7ET, United Kingdom
T: +44 121 204 3381; F: +44 121 204 3680; E: a.v.bridgwater@aston.ac.uk

ABSTRACT

A biorefinery can be considered as the optimised performance of the use of biomass for materials, chemicals and energy applications. Performance relates to the following measures, but as these are not necessarily compatible or consistent in defining the best process system, optimisation usually requires their careful consideration:

- Carbon balance
- Cost
- Environment
- Impact
- Social aspects
- Yield

Bio-refineries have existed for many years, although the term biorefinery is relatively recent. Pulp and paper mills are one example, but there are many instances where fuels and chemicals have been co-produced such as RME plants where glycerine is co-produced with RME; bio-ethanol plants from ligno-cellulosics where lignin is used as a fuel and as a source of chemicals; food flavourings from pyrolysis of biomass where the resides are used as a fuel or a source of other chemicals.

In many examples, co-production of energy products or chemicals results from the requirement to dispose of wastes or byproducts in a satisfactory way. It is only relatively recently that the potential for optimised co-production of valuable products has been fully appreciated and strongly promoted, which has given rise to the concept of a biorefinery. Polygeneration is a European Commission term with the same connotations – the optimised production of fuels and chemicals.

This paper focuses on fast pyrolysis of biomass as the core of a system to optimise the use of biomass. This paper summarises the characteristics and advantages of pyrolysis forming the core of a biorefinery and outlines some scenarios in which the unique features of fast pyrolysis can be effectively exploited. Consideration is given to concepts based only on pyrolysis and pyrolysis products, concepts that broaden the scope to encompass other downstream processes and finally concepts in which pyrolysis can make a valuable contribution within the broader context of utilisation of biomass.

CARGILL'S VIEW OF BIOREFINERIES - THE REVOLUTION HAS BEGUN

Jim Stoppert

Cargill, 15407 McGinty Rond West, MS 69, Wayzata, MN 55391
(952) 742-5488: jim_stoppert@cargill.com

Abstract

Cost and technology have been the critical issues to be resolved in the path towards the bio revolution. Higher cost and unstable hydrocarbons have caused an acceleration down the path that will result in an earlier commercialization than many anticipated.

PROGRESS IN COMMERCIALIZATION OF POLYOL CHEMICALS FROM CORN

A. T. BRIX,
International Polyol Chemicals Inc, Blue River, OR 97413,
ATBrix@Earthlink.net,

TEITUR GUNNARSSON, IPCI Engineering
HONGBIN QI, Global Biochem

International Polyol Chemicals Inc. and its development partner Icelandic Green Polyols (hereinafter Polyol Partners) have developed a continuous catalytic process for the conversion of monomer sugars (glucose) to industrual glycols (ethylene glycol, propylene glycol and butanediols).

In concert with Global Biochem of China the Polyol Partners and GBT have built a 10,000 MT glycol facility in Changchun, China at the site of Global's main corn processing facility. Currently the partners are constructing a 200,000MT facility in Changchun. The paper outlines the process, general process economics and the future for green sugar based glycols.

BIOREFINERIES AND BIOFUELS: CURRENT ACTIVITIES AND FUTURE VISION OF PETROBRAS

Luiz Fernando Leite, João Norberto Noschang Neto, Juliana Vaz Bevilaqua

Petrobras R&D center, Av. Jequitibá n.950, Ilha do Fundão, Rio de Janeiro, Brazil, CEP 21949-900
lleite@petrobras.com.br

Introduction

PETROBRAS has been increasing its oil production and should reach 1.9 million bpd in Brazil, of which 75% will be produced from deep and ultra-deepwater reservoirs, accordingly the country will be very close to its oil self-sufficiency. The domestic crudes are heavier than normal imported ones, resulting in a higher yield of vacuum residue production. It is a sweet crude but contains more nitrogen compounds, which impair the yields of the refining catalytic process, due to the basic nitrogen species. Moreover the asphaltene content and naphthenic acidity levels are higher and the latter contaminant increases the corrosion problems in refining installations. Table 1 shows the main characteristics of domestic crudes compared to an imported one, the Arabian Light. There are also some heavy crude oils that come from onshore production areas, like Fazenda Alegre also shown in the table.

Table 1. Oil crude data

	Arabian Light	Cabiúnas	Marlim	Fazenda Alegre
º API	33.30	24.70	19.70	13.2
S (%w/w)	1.63	0.47	0.75	0.31
N (%w/w)	0.09	0.27	0.45	0.33
Asphaltenes (%w/w)	1.10	2.80	2.60	7.3
Metals (ppm)				
Ni	3.50	9	19	42
V	14	12	24	6
TAN (mg KOH/g)	< 0,05	0.51	1.23	0.8

The heavier crudes generate a greater volume of fuel oil, a lower added value product. For environmental issues, there is a trend of increasing the natural gas domestic consumption displacing the fuel oil market demand. This magnifies the need for a higher conversion to keep the balance of product demand / offer. PETROBRAS in particular has the additional challenge of matching the increasing supply of Brazilian oil with the need of producing diesel and gasoline with a more stringent specification concerning quality and environmental aspects. These required conversion units, as well as, the hydrotreating units needed in the future refining scheme to meet better fuel quality are very energy demanding processes, worsening the greenhouse gas emissions problems at refineries.

Biodesulfurization and biodenitrogenation

An option for upgrading the quality of the crude oil and the refining of its intermediary streams is to make bio-treatments, using microorganisms capable of removing sulfur, nitrogen and heavy metals. Compared with conventional technologies the bio-refining presents the following advantages: much less severity - requiring close to ambient operational temperature and pressures; lower energy consumption; no hydrogen demand – the hydrogen balance at refineries little by little is becoming more critical due to the high quality fuels requirement; and yet the product volume is preserved. On the other hand, there are some drawbacks in applying this kind of technology, such as: low concentration of microorganism aqueous solutions; low reaction rates; complementary technology; specific solution; and far removed from the refiner culture.

Furthermore there are some technological challenges still to be overcome, such as: high efficiency and stable bio-catalyst; high biomass production – high microorganism reproducibility; conceptual process – careful handling of microorganism solutions; bio-safety.

A bacterial strain F.5.25.8 (*Gordonia amicalis*) was cultivated, which presented good conversion from dibenzothiophene to 2-hydroxybiphenil, via the 4S pathway. This culture seems to be unique because it can simultaneously cleave carbon-sulfur and carbon-nitrogen bounds, removing both contaminants from typical petroleum streams. *Pseudomonas nitroreducens* strain can perform the quinoline degradation and was able to grow using this product as the only nitrogen source. Therefore some progress was obtained in the lab scale phase and a pilot facility is being built to up- scale this process phase.

Biofuels

Despite of the increasing in crude oil production and its oil reserves, PETROBRAS has changed its strategy and is positioning itself not only as a petroleum player but as an integrated energy company. In this sense it is broadening its activities to other energy source besides fossil fuels. One of the areas of increasingly grow is energy from renewable resources.

Alcohol. Brazil is the world's mayor ethanol producer from sugar cane, with a broad domination of the production chain considering the agriculture and industrial aspects. The production was 13 million m3 in 2004 and this is expected to expand to about 14 million m3 in 2006. The country has some competitive advantages, as the crop presents a high sucrose content and the seasonal conditions allows the production all year round, as the harvest in the Northwest region takes place from October to March and in the Center-South from April to December. This reduces the logistic and storage costs, therefore Brazil has the lowest alcohol cost production on a worldwide basis. It also is in a lead position in relation to bio-fuels application, as ethanol has been utilized for powering the domestic light vehicles fleet since 1975, when the National Alcohol Program was created. Today the Brazilian light vehicle fleet is powered by ethanol or gasohol, as a legal requirement a typical mixture is 24% ethanol plus 76% gasoline, so this rules out any chance of using an alcohol free fuel in the country.

PETROBRAS had a critical participation during the alcohol program implementation, offering its logistic assets for ethanol distribution all over the country and supported engine performance tests of gasoline plus ethanol fuel blending. The Company has a long experience in handling and commercializing this product. Moreover, in the eighties, PETROBRAS carried out the development of the Ethanol Production from Cassava technology, reaching a technical-economical production line, which was commercially applied but unfortunately wasn't a successful enterprise, due to the failure of the agricultural project.

Biodiesel. Biodiesel is a renewable fuel with clear social and environmental benefits, associated to man's fixation of rural areas, generation of work and income, and the minimization of gas

emissions that contribute to global climatic changes. Strategically biodiesel is also seen as a diversification from traditional energy patterns, mainly for those countries that import mineral diesel. This fuel composed of mono-alquil esters of long chain fat acid obtained from vegetable oils or animal fats, known as biodiesel, can bring some advantages such as higher lubricity and higher cetane numbers, bringing improvements in ignition quality. With the government regulatory standard already established, the search for good quality biodiesel production represents a technical, economical, social and environmental challenge.

The development of the technological process, with the best chosen oleaginous raw material and alcohol to be used for the esterification step, poses a difficult puzzle to solve. New production processes nurtured in the laboratory, must be up-scaled if they are to become commercially viable and the producers don't opt to import technology from the established markets. Furthermore another important technical aspect is the choice of alcohol, because worldwide biodiesel is produced with methanol and so Brazil's great challenge is the use ethanol and to make it achieve the same performance.

It is well known that around 85% of the biodiesel overall cost is directly related to the raw material cost: the seed or the vegetable oil. Given all the possibilities, Brazil has a vast number of options: castor bean, soy bean, turnip, domestic pine, babassu coconut, palm coconut, sunflower, peanut, cotton and a series of other oleaginous products. Not to mention bovine fat and used cooking oil among others. Brazil is a prominent country in the world scenario of bio-fuels, because of the previously cited huge alcohol production, as well as, climate conditions and favorable soil for growing biomass and the cultivation of different oleaginous products.

PETROBRAS is developing two parallel R&D projects: the first one, the trans-esterification process is starting directly with the oleaginous seed in the presence of a catalyst and ethanol. This process, patented by PETROBRAS, was validated in the laboratory, tested in a Pilot Plant and now is being up-scaled, via the implementation of a Prototype unit that should start its operation in the forthcoming November. The other project, a more conventional one, is the reaction of vegetable oils with ethanol in the presence of a catalyst for the corresponding ester production. PETROBRAS has recently applied for the process and equipment patents. The process was also developed in the laboratory, tested in a Pilot Plant scale and will be checked in a semi-industrial unit soon.

Biorefineries

The search for alternative sources of energy has become part of the priorities of the modern society, principally renewable. Therefore the biorefineries, i.e., a biomass based facility for producing products is in the spotlight. In the Brazilian scenario, it would be more economically sound to revamp and upgrade the existing Alcohol Distilleries, thus transform them into an integrated sustainable energy and fuels production unit. Nowadays only one third of the energy that could be obtained from sugar cane crop is actually used. From the alcohol production obtained from sugar cane, the residual bagasse can be used for electric power generation, as is done though inefficiently today, as well as, for a secondary production of alcohol, via its hydrolysis and fermentation. Furthermore through improved mechanical harvesting the sugar cane leaves can also be collected and chopped, instead of just being burned in-situ or just left to rot, from which other products can be obtained. The resultant straw can be used for energy generation, via burning, or be applied for more added-value products, such as: ethanol (through the conversion of lignocellulosic materials) and other hydrocarbons (by means of gasification and Fischer-Tropsch synthesis). PETROBRAS is developing technologies to produce ethanol from lignocellulosic materials either using acid and enzymatic hydrolysis. PETROBRAS is also developing alternative processes to conventional fermentation by means of Simultaneous Saccharification and fermentation (SSF).

As a matter to improve biodiesel co-products value, PETROBRAS has resume the know-how in producing ethanol from starch materials (cassava) and developed a process that intent to detoxify and produce ethanol from castor bean cake. The process employs acid hydrolysis and conventional fermentation and produces over 100 L of ethanol from each ton of castor bean cake. That way, it is possible to add value to the residual cake and reduce biodiesel production costs. The process is still in lab scale and soon will be scaled up.

These materials that are being tested for ethanol production have low market value and otherwise would be wasted. From the results achieved, it is possible to foresee integrated units where from oleaginous raw material it is possible to produce biodiesel with minor material inputs and waste outputs.

INTERCEPTED HYDROLYSIS STRATEGIES FOR BIOMASS REFINERIES

J. Michael Robinson, Jessica Burrow, Robert Caudle, Luis Galvan

Chemistry Department
The University of Texas of the Permian Basin
4901 East University Blvd.
Odessa, TX 79762

Introduction

Massive historical efforts to fractionate biomass into monomeric aldose sugars have not achieved high yields in a commercial manner. Lack of success has been attributed to the very complex nature of various biomass resources, severe conditions required, concomitant degradation reactions, lack of reagent selectivity between biomass components, and commercially impractical reactors. At the heart of the biomass hydrolysis problem is the inherent reactivity of the aldose sugar products required for fermentation into ethanol. Rather than aldoses, products more stable to the hydrolysis conditions had to be considered to solve this hydrolysis problem.

Indeed, recent intercepted hydrolysis strategies that instantaneously convert aldoses into different functional groups have been shown to solve this problem. As shown in Fig 1, conducting either simultaneous reduction, or oxidation, with the hydrolysis allows facile conversion of the incipient aldehyde into either alcohol or acid functional groups, respectively. While useful chemicals are formed directly from such intercepted hydrolyses, chemical reaction processes rather than fermentations are then utilized to produce fuels and other chemicals in a biomass refinery scheme.

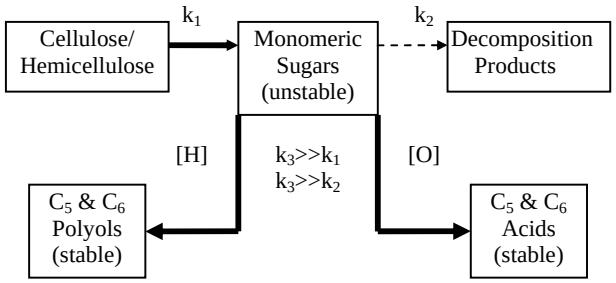


Figure 1. Oxidative and Reductive Intercepted Hydrolysis Strategies

Results and Discussion

Figure 2 illustrates a completely integrated biomass refinery Scheme that uses a reductive intercepted hydrolysis strategy and subsequent chemical reduction processing methods.

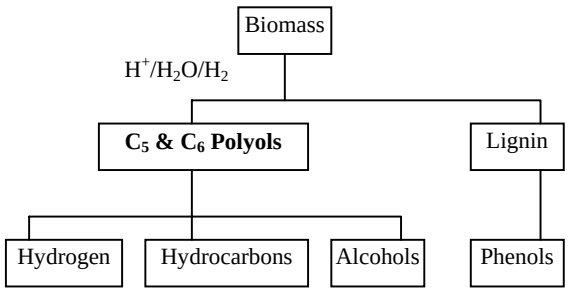


Figure 2. Reductive Intercepted Hydrolysis Scheme

Conducting a "intercepted dilute acid hydrolysis and hydrogenation" (**IDAHH**), provides a solution of polyols (xylitol, sorbitol), rather than aldoses (xylose, glucose), quantitatively fractionated from lignin solids.[1] Conversions approaching the theoretical amounts are obtained with wood sawdust in 3-6 hr at <190 °C with 0.8% H_3PO_4. The dual slopes of the rate of hydrogen consumption shown in Fig. 3 indicate correspond to the easily hydrolyzed hemicellulose versus the slowly reacted crystalline cellulose. With the ideal yield of polyols containing no detectible phenols, this is a remarkably clean fractionation from lignin. Lignin is subsequently converted into phenols.

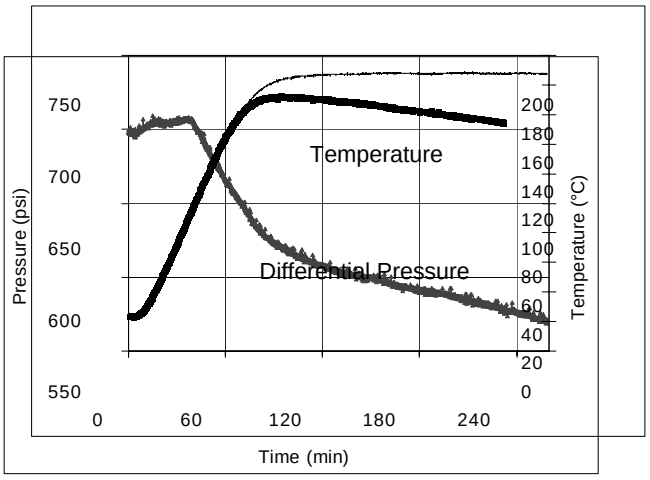


Figure 3. Hydrogen Consumption Curve for Pine Sawdust.

We have established a *chemical* process (Fig. 4) for the production of various hydrocarbon fuels and chemicals from biomass derived polyols.[2,3,4] Polyols are converted into mainly liquid hydrocarbons by reduction with boiling hydriodic acid. Hydrocarbons phase separate and the aqueous acid is recycled. A second step converts remaining halocarbons into alkenes. An electrochemical regeneration of the primary reducing solution provides an economically improved process and is the subject of a new patent application. C_{12} alkenes can be hydrogenated to increase octane rating from 78 to ~83 AKI and hexenes may be hydrogenated to solvent grade hexane for seed oil extraction.

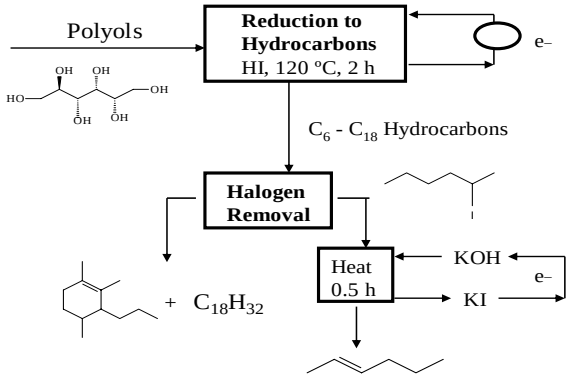


Figure 4. Polyols to Hydrocarbons Process

Polyols are also converted by other means into hydrogen, or small alcohols. Dumesic's process can produce hydrogen from monomeric sugars and the preferred substrate is indeed polyols.[5] Biomass derived hydrogen can perhaps best be used internally in our refinery to initially fractionate biomass and in subsequent reactions as well. Additionally, mixtures of methanol and ethanol can be obtained by catalytic hydrogenolysis using 5% H_2SO_4 and Ru/C at 200 ^oC.[6]

Similarly, a selective oxidation hydrolysis strategy achieves polyhydroxy acids in solution apart from lignin, Fig. 5. Aldonic acids are selectively reduced into high octane oxygenate fuel additives, lactones with 108 and 113 AKI.[7] Polymers and other products may also be produced.

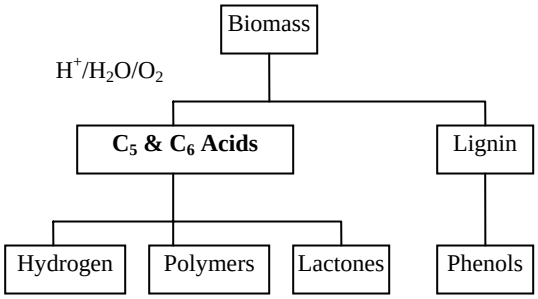


Figure 5. Oxidative Intercepted Hydrolysis Scheme

Polyols and aldonic acids provide alternative "sugar platforms" for biomass conversion to hydrocarbon fuels and solvents, alcohols, lactone fuel additives, hydrogen and other chemicals. Economic estimates from engineering models of these intercepted hydrolysis schemes and products will also be presented.

Acknowledgements

The Robert A. Welch Foundation Chemistry Department Grants, a National Renewable Energy Lab contract, a U.S. Department of Energy Basic Energy Sciences - Advanced Research Projects grant, and the Texas Higher Education Coordinating Board - Advanced Technology Program have supported this research.

References

1. Robinson, J. M.; Burgess, C.E.; Bently, M.A.; Brasher, C.D.; Horne, B.O.; Lillard, D.M.; Macias, J.M.; Mandal, H.M.; Mills, S.C.; O'Hara, K.D.; Pon, J.T.; Raigoza, A.F.; Sanchez, E.H.; Villarreal, J.S. *Biomass and Bioenergy*, **2004,** *26(5),* 473-483.
2. Robinson, J.M.; Burgess, C.E.; Mandal, H.D.; Brasher, C.D.; O'Hara, K.O.; Holland, P.L. *Amer. Chem. Soc. Fuel Chem. Div. Preprints* **1996**, *41(3),* 1090-1094.
3. Robinson, J.M. U.S. Patent 5,516,960, **1996**.
4. Robinson, J.M.; Banuelos, E.B.; Barber, W.C.; Burgess, C.E.; Chau, C.; Chesser, A.A.; Garrett, M.H.; Goodwin CH, Holland PL, Horne BO, Marrufo LD, Mechalke EJ, Rashidi JR, Reynolds BD, Rogers TE, Sanchez, E.H.; Villarreal, J.S. *Amer. Chem. Soc. Fuel Chem. Div. Preprints* **1999**, *44(2),* 224-228.
5. Cortright, R.D.;.Davda, R.R.; Dumesic, J.A. *Nature* **2002,** *418*, 964-967,
6. Abreu, C.A.M.; Lima, N.M.; Zoulalian, A. *Biomass and Bioenergy* **1995**, *9*, 487-492.
7. Robinson, J.M. U.S. Patent pending , **2004**.

MEASURING CELLULASE ACCESSIBILITY OF DILUTE-ACID PRETREATED CORN STOVER

Tina Jeoh, David K. Johnson, William S. Adney and Michael E. Himmel

National Bioenergy Center, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401

Introduction

To enable a new biorefinery industry, lignocellulosic biomass must be cost effectively hydrolyzed to fermentable sugars. Biomass recalcitrance is defined as the natural resistance of this substrate to the action of cellulases and other polysaccharidases. In order to maximize the fermentable sugar stream from corn stover, a dilute-acid pretreatment step has been used traditionally to facilitate enzyme access to the cellulose fraction. A key factor for successful enzymatic digestion of lignocellulosic biomass is providing cellulase enzymes access to the β-(1→4) glycosidic bonds of microcrystalline cellulose. Any effective pretreatment of the biomass feedstock; therefore, must increase accessibility of cellulases to the cellulose fraction in the cell wall microfibrils. The specific physical properties of biomass that are thought to hinder cellulase accessibility include the hemicellulose-containing microfibril sheath[1] and the lignin rich[2] structures in the cell wall.

Trichoderma reesei Cel7A, a cellobiohydrolase that is extremely efficient on crystalline cellulose, is the "workhorse" of the *Trichoderma* cellulase system, constituting 60% of the cellulase protein secreted by the fungus. In this study, we report the effectiveness of dilute-acid pretreatment of corn stover on improving accessibility to cellulases using fluorescence-labeled, purified *T. reesei* Cel7A as a probe.

Experimental

Substrate preparation. The samples used in this study were produced from corn stover collected from Pioneer 34M95 maize harvested in Colorado in 2002. Corn stover aliquots were subjected to thermal chemical pretreatment in NREL PDU's pilot-scale vertical reactor using a fixed residence time of approximately 1 min at temperatures ranging from 180-200ºC; solid loadings between 20-35% (w/w); and acid loadings of 0.03-0.06 g acid/g dry biomass. The pretreated corn stover samples used in this study were provided by Dan Schell (NREL). Raw corn stover was Wiley-milled to 200 mesh and hydrated with 5 mM sodium acetate buffer, pH 5.8 under vacuum. Sodium azide (0.2%) was added after re-hydration. Pretreated corn stover (PCS) samples were washed repeatedly with several exchanges of distilled water and stored in 5 mM sodium acetate, pH 5.0 with 0.2% sodium azide. The concentrations of the PCS suspensions were established by determination of oven-dry weights on triplicate 1.0 mL samples.

Enzyme Preparation. *T. reesei* Cel7A was purified from Spezyme CP (Genencor International) by the following procedure. Spezyme CP was loaded onto a Resource Q anion exchange column (Amersham Biosciences) and eluted with a linear gradient of 0 to 1.0 M NaCl in 20 mM BisTris, pH 5.8. The fractions with activity on *p*-nitrophenyl-β-D-lactopyranoside (*p*NPL) were pooled, concentrated in an Amicon concentrator with a PM-10 membrane (Millipore), spiked to a final concentration of 1 mM gluconolactone, and loaded on a *p*-aminophenyl-β-D-cellobioside (*p*APC) affinity column[3]. Bound protein was eluted as a major peak (indicated by absorbance at 280 nm) with 10 mM cellobiose in 100 mM sodium acetate buffer with 1 mM gluconolactone (pH 5.0). When applied to SDS-PAGE, an aliquot from the chromatographic peak yielded two bands, one corresponding to Cel7A and the other to a higher mobility band corresponding to the molecular weight (MW) of the catalytic domain. The unbound fraction and the wash fractions were concentrated and examined by SDS-PAGE, which indicated the presence of a band corresponding to Cel7A. All fractions containing Cel7A were pooled, spiked with a final concentration of 1.0 M ammonium sulfate, and loaded on a HiLoad 16/10 phenyl-sepharose hydrophobic interaction column (Amersham Biosciences). The bound protein was eluted with a linear ammonium sulfate gradient decreasing from 1.0 M to 0 M in 20 mM BisTris buffer, pH 5.8. Fractions with activity on *p*NPL were pooled and concentrated. On SDS-PAGE gel, the concentrated protein solution showed a single band with MW corresponding to *T. reesei* Cel7A. Cel7A was labeled with Alexa Fluor 594 succinimidyl esters (Invitrogen) according to the manufacturer's recommended protocol.

Cellulase accessibility experiments. Cellulose accessibility of the raw and pretreated corn stover samples was determined with purified, Alexa Fluor 594 labeled *T. reesei* Cel7A. The experiments were conducted in triplicates, with each sample containing 1.0 μM *T. reesei* Cel7A and PCS concentration equivalent to 1.0 mg/mL final cellulose concentration. Final reaction volume was 250 μL in 5 mM sodium acetate (pH 5.0). The reactions were conducted at 38ºC, rotating end-over-end and assayed at 1, 4, 24, 48 and 120 hours. For select samples, 5-minute reactions were conducted in a 38ºC water bath and agitated manually for the duration of the reactions. Enzyme and substrate used in the 5-minute reactions were pre-incubated at 38ºC for a minimum of 30 minutes. Each reaction was initiated with the addition of the enzyme and terminated by filtration through 1.0 μm glass fiber filters in a 96-well vacuum filter manifold (Innovative Microplate). The reaction supernatant was assayed for reducing sugars using the BCA method[4] against a cellobiose standard curve. The bound enzyme fraction was assayed by fluorometry as described previously[5]. The solid fraction retained in the filter was re-suspended with 250 μL distilled water and transferred to a 96-well microtiter plate. A set of *T. reesei* Cel7A standards was included with each microtiter plate for the standard curve. PCS was added to the wells with Cel7A standards to match the reaction samples. The plates were read in a FLUOstar OPTIMA (BMG Labtechnologies) plate reader at excitation/emission wavelengths of 584/612 nm.

Results and Discussion

The range of pretreatment conditions applied to this set of corn stover samples resulted in the removal of 67 - 97 % xylan, with higher xylan removal resulting from higher pretreatment severities. Up to about 85 % xylan removal, there was a strong correlation between the cellulose conversion after 5 days of incubation with *T. reesei* Cel7A and the extent of xylan removal (Fig. 1).

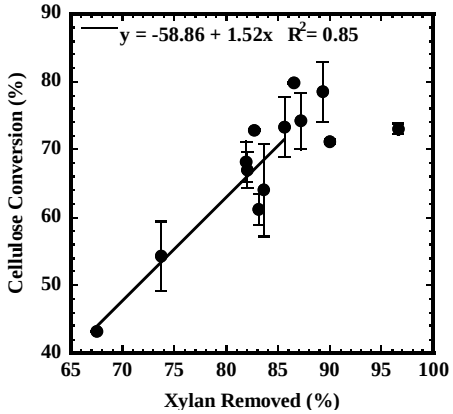


Figure 1. PCS cellulose conversion at 120-hours with respect to xylan removal.

The data in Fig. 1 suggests that removing up to 85 % of the xylan facilitates cellulase access to the cellulose fraction in corn stover. To study this further, bound enzyme concentrations were measured over the hydrolysis time course. At 1-hour, we observed higher bound Cel7A concentrations for PCS samples with higher extents of xylan removal (Fig. 2), indicating that removal of xylan from the biomass does indeed allow more cellulases to adsorb.

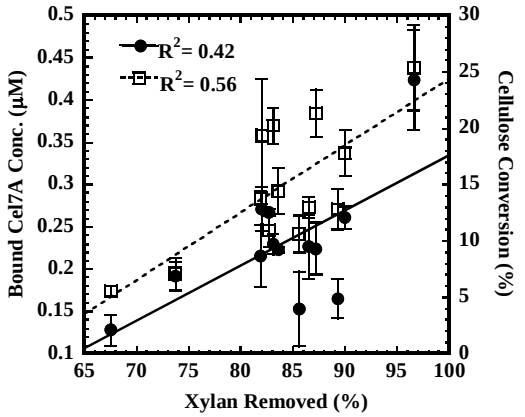


Figure 2. Concentration of Cel7A bound to PCS and cellulose conversion after 1-hour incubation at 38°C. (●) bound Cel7A concentrations, (□) cellulose conversion.

Furthermore, higher concentrations of adsorbed Cel7A facilitated higher cellulose conversions (Fig. 2).

The question of the effect of diffusion through the biomass matrix by Cel7A was studied by measuring the bound enzyme concentration after incubation for 5 minutes on select samples. Logistically, five minutes was the shortest reaction time possible to obtain reliable data. As shown in Fig. 3, the concentration of bound Cel7A did not change significantly from 5-minutes to 1-hour.

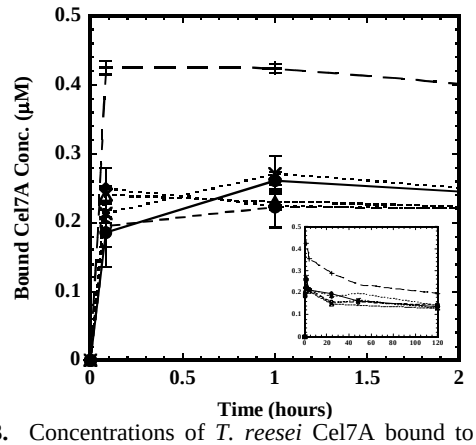


Figure 3. Concentrations of *T. reesei* Cel7A bound to PCS at 5-minutes and 1-hour. Inset shows data for 120-hour reaction period for the same sample set. Samples shown have 82 - 97 % xylan removed. Lines are drawn only to guide the eye.

The inset graph in Fig. 3 also shows that the bound concentrations decreased with reaction time over the full 5-day reaction period. The data therefore suggests that the maximum possible bound cellulase concentration is achieved rapidly and access to cellulose by the enzyme is not limited by diffusion.

The lignin component in biomass is often cited as decreasing the effective cellulase concentration in the system by acting as an adsorbent[6]. The raw corn stover samples contained 11.4% lignin on a dry weight basis. As the dilute-acid pretreatment did not remove any lignin, with the loss of the hemicellulose fraction, final lignin content of the PCS samples was in the range of 29-38%. After 120-hours incubation with Cel7A, 43-78% of the cellulose was hydrolyzed. Yet, in most of the samples, less than 15 % of the total cellulase remained bound by the end of the reaction (Fig. 4).

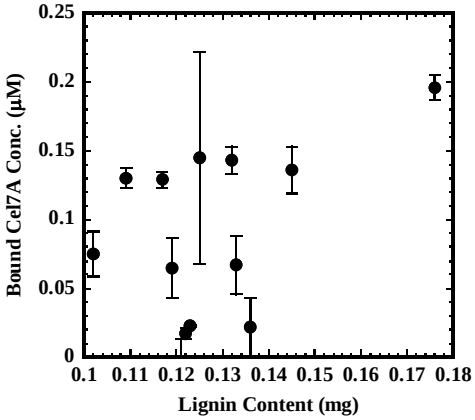


Figure 4. Concentration of Cel7A bound to PCS at 120-hours with respect to the amount of lignin in the reactions (Total Cel7A concentration in each reaction was 1.0 μM).

Furthermore, no correlation was observed between the amount of lignin present in the reactions and the concentration of bound Cel7A at 120-hours. This result supports a previous observation where the activity of *T. reesei* cellulases on pure cellulosic substrates was not inhibited by the addition of a lignin-rich biomass residue[7].

Conclusions

It is known that the extent of xylan removal from corn stover by dilute-acid pretreatment increases with higher severities, with minimal change in the amount of lignin. The effect of these changes on the accessibility of the cellulose fraction to cellulases was examined and our results indicated that cellulase-cellulose interactions were enhanced by this pretreatment. Higher extents of xylan removal resulted in greater cellulase adsorption and higher overall cellulose conversions. Adsorption of Cel7A was not diffusion-limited. Furthermore, *T. reesei* Cel7A appears to have a low affinity to lignin, thus biomass recalcitrance in this case is most likely not due to loss of this cellulase via adsorption to lignin.

Acknowledgement. The authors wish to thank the US DOE Office of the Biomass Program for funding this work.

References

(1) Irwin, D. C.; Cheng, M.; Xiang, B. S.; Rose, J. K. C.; Wilson, D. B., *European Journal of Biochemistry*, **2003,** *270*(14), 3083-91.
(2) Kim, T. H.; Kim, J. S.; Sunwoo, C.; Lee, Y. Y., *Bioresource Technology*, **2003,** *90*(1), 39-47.
(3) Sangseethong, K.; Penner, M. H., *Carbohydrate Research*, **1998,** *314*(3), 245-50.
(4) Kongruang, S.; Han, M. J.; Breton, C. I. G.; Penner, M. H., *Applied Biochemistry and Biotechnology*, **2004,** *113-16*, 213-31.
(5) Jeoh, T.; Wilson, D. B.; Walker, L. P., *Biotechnology Progress*, **2002,** *18*(4), 760-9.
(6) Converse, A. O.; Ooshima, H.; Burns, D. S., *Applied Biochemistry and Biotechnology*, **1990,** *24-5*, 67-73.
(7) Meunier-Goddik, L.; Penner, M. H., *Journal of Agricultural and Food Chemistry*, **1999,** *47*(1), 346-51.

MEASUREMENT OF POROSITY IN DILUTE ACID PRETREATED CORN STOVER

Claudia Ishizawa, Mark Davis and David K. Johnson

National Renewable Energy Laboratory
1617 Cole Blvd., Golden, CO 80401-3393

Introduction

Pretreatment has been established as an essential process to increase the susceptibility of lignocellulosic materials to the action of cellulolytic enzymes. The degree of chemical and/or physical modification of the substrate varies with the source and type of feedstock, as well as with the pretreatment conditions. Pretreatment can alter the structure, composition, surface and reactivity of biomass. Considerable interest exists in developing fast and reliable methods to measure these properties and to correlate them with the performance of the material during enzymatic hydrolysis.

Several workers have found good correlations between porosity and the enzymatic digestibility of cellulose in pretreated biomass[1,2]. However, the characterization tools commonly used on porous materials, i.e., electron microscopy, gas adsorption, and mercury porosimetry, are not useful on biomass because they require dry samples and drying frequently causes collapse of the pore structure. Attempts to prepare dry fibers with undamaged pores have not met with great success. From the literature, two methods for wet-fiber characterization were identified: the solute exclusion technique[3] and thermoporosity by NMR[4]. In this work, the applicability of these methods to the study of corn stover after dilute sulfuric acid pretreatment was evaluated.

Experimental

Pretreated Corn Stover. The samples used in this study were produced from corn stover collected from Pioneer 34M95 maize harvested in Colorado in 2002. The corn stover was subjected to dilute acid pretreatment in NREL PDU's pilot-scale vertical reactor using a fixed residence time of approximately 1 min at temperatures ranging from 180-200ºC; solid loadings between 20-35% (w/w); and acid loadings of 0.03-0.06 g acid/g dry biomass. The compositions, cellulose enzymatic digestibilities, and ethanol yields potentials for these samples was measured previously. Following pretreatment, samples were stored at 4ºC and pH~1. Prior to use, the samples were thoroughly washed with distilled water until the wash was colorless and neutral in pH. After the last washing the samples were filtered into a press cake of approximately 20% (w/w) solids. The pretreated corn stover samples were provided by Dan Schell (NREL).

Solute exclusion method. The accessible pore volumes of ToyoPearls (commercial chromatographic resins), unpretreated corn stover, and pretreated corn stover were determined by the solute exclusion technique of Stone and Scallan[3]. This technique measures the accessible pore volume in water-swollen materials using a series of molecules of known molecular size (molecular probes).

A series of dextrans (obtained from Serva Electrophoresis GmbH), polyethylene glycols (from Sigma-Aldrich and JT Baker), and analytical grade glucose were selected as probe molecules. About 1.0 g of ToyoPearl or 0.5 g of corn stover was weighed into a tared plastic snap cap centrifuge tube, and 1 g of 1.0% (w/v) probe solution was added. The tubes were periodically hand shaken for about 30 s during 2-3 h. After this time, the solution was filtered using a 0.45µm nylon filter, transferred, and then sealed into HPLC vials for analysis. The solids were washed and dried at 105ºC to determine dry solid weights. Three replicate samples were prepared for each solution. A distilled water blank was prepared for each pretreated corn stover.

The concentration of molecular probe in the filtered liquids was measured using an Agilent 1100 HPLC equipped with a refractive index detector. The HPLC was run without a column and with a simple union fitting between the injector and the detector. The eluent was nanopure water at a flow rate of 0.4 ml/min. The injection volume was 10 µl and analyses were repeated 4-5 times for each sample.

The inaccessible water expressed as milliliters of water per gram of dry substrate, can be calculated using the following equation[1]

$$d_i = \left(\frac{W+q}{p}\right) - \left(\frac{W}{p}\cdot\frac{C_i}{C_f}\right)$$

where d_i is the inaccessible water (ml/g) for solute of size i; W is the mass of solution; q is the mass of water in sample of solids; p is the dry mass of the sample; C_i is the initial solute concentration; and C_f is the final solute concentration.

The accessible pore volume (A_i) for a solute of size i is given by

$$A_i = d_{560} - d_i$$

where d_{560} represents the total water volume in the substrate.

Thermoporosity. This method uses the changes in the physical properties of a liquid when it is confined within small pores. In particular, the melting temperature of the liquid is depressed and related to the pore distribution through the Gibbs-Thompson equation[4]

$$\Delta T = \frac{K}{r}$$

where ΔT is the melting point depression of the liquid; K is a constant depending on the characteristics of the material; and r is the pore dimension.

Two techniques have been extensively used to observe the freezing-melting behavior of water in confined pores: differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR). DSC measures the heat transfer, whereas NMR records the fractions of frozen and unfrozen liquid as a function of temperature.

In this study, we report results obtained using NMR spectroscopy. The ^{1}H NMR experiments were conducted with a Varian Unity 300 MHz (7.0T) spectrometer. The spectra were collected using a $\pi/3$ pulse and a 5s recycle delay. For each experiment, approximately 0.8-1.2 g of undried corn stover was introduced into a 10mm NMR tube. The sample was cooled to 230K and then the NMR signal of the unfrozen water was recorded at intervals of 10K until 285K was reached. Samples were allowed to equilibrate for 5-8 minutes at each temperature. At 285K, the signal is directly proportional to the total amount of water in the sample, and at temperatures below 273K, the signal is proportional to the weight of unfrozen water. The pore volume per g of biomass was then calculated by dividing the signal at lower temperatures by the signal at 285, multiplying by the total weight of water in the sample, and dividing by the dry weight of the sample.

Results and Discussion

The solute exlusion method was validated before it was applied to the measurement of the porosity of pretreated biomass samples. Four different chromatographic resins of known porosity were selected as standards. The particle sizes and pore sizes of the ToyoPearl resins are summarized in Table 1.

Table 1. PROPERTIES OF TOYOPEARL RESINS*

ToyoPearl	Particle size (µm)	Pore size (Å)
HW-40S	20-40	50
HW-40C	50-100	50
HW-50F	30-60	125
HW-55S	20-40	500

*from the manufacturer

In Figure 1, the accessible pore volume and the pore size distribution curves for the ToyoPearl resins are shown. The error bars indicate the magnitude of one standard deviation of the volume accessible to individual probes, from 3 measurements in each case.

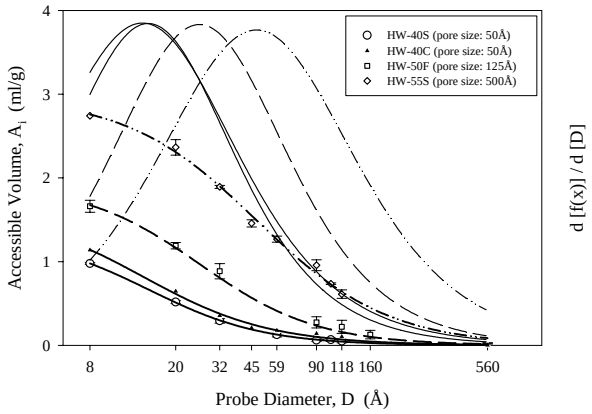


Figure 1. Accessible pore volume and pore size distribution curves for ToyoPearl resins.

From the results, it is easy to distinguish between the different pore size resins. Two resins had the same pore size distributions but different particle size, and we can observe that the measurements are not affected by the particle size.

After testing and verifying the solute exclusion method with the ToyoPearl resins, the same conditions were used to determine the porosity of pretreated corn stover. Figure 2 shows data from the measurement of accessible pore volume in pretreated corn stover compared to the accessible pore volume in unpretreated corn stover.

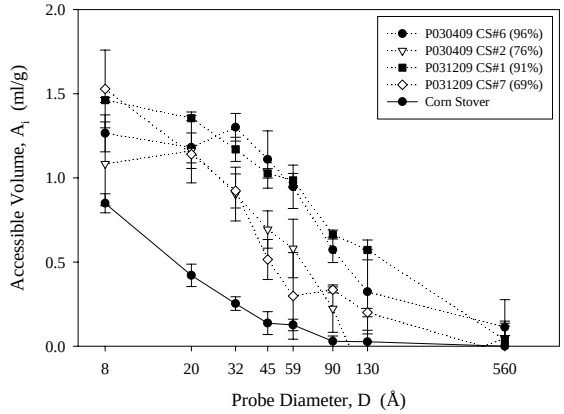


Figure 2. Accessible pore volume of unpretreated corn stover and pretreated corn stover. Ethanol yield are indicated in parenthesis.

The results show that there is significantly less accessible pore volume in the unpretreated corn stover compared to that in the acid pretreated samples, in particular in the range from 10 to 100 Å. However, it is clear that the differences in accessible pore volume in the selected pretreated samples cannot be detected because of the poor reproducibility of the measurements. The variability of the measurements is higher with the pretreated corn stover samples than with the Toyopearl resins; an explanation for this can be the higher level of heterogeneity in the pretreated corn stover.

Typically the effectiveness of a pretreatment is judged by the level of hemicellulose hydrolysis or more simply by the extent of xylan removal. High levels of xylan removal normally indicate effective pretreatment and that the cellulose will be relatively easily saccharified using cellulase enzymes. The solute exclusion method showed differences in the accessible pore volume between the unpretreated and the pretreated corn stover, but only very small differences were observed amongst the pretreated samples that gave from 70 to 96% ethanol yields. A poor correlation was found between the accessible volume and cellulose digestibility.

NMR thermoporometry represented an alternative method to measure the total pore volume in the range of 20 to 200Å. Using the Gibbs-Thompson equation a relationship between temperature and pore size can be established. It was found that a melting temperature for water of 240 K corresponds to a pore size of 20 Å, whereas 270 K corresponds to 200 Å. In Figure 3, the intensity vs. inverse of temperature (IT) curve for unpretreated and four pretreated corn stover samples, and water are shown.

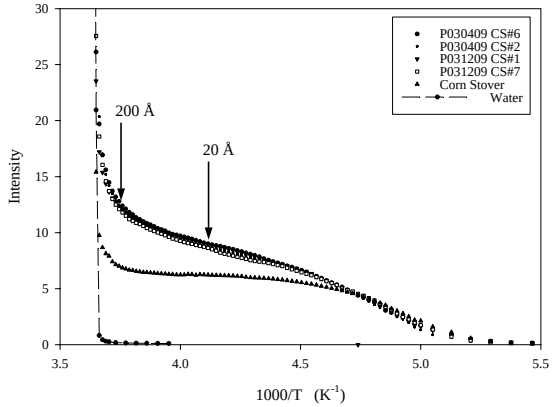


Figure 3. IT-curve for unpretreated and pretreated corn stover, and water.

The curves exhibit similar results to those obtained with the solute exclusion method. All pretreated samples showed a larger porous structure than the starting corn stover material. However, no significant difference was found between the pretreated corn stover samples that produced different ethanol yields.

Conclusions

The solute exclusion method was successfully validated with four standards of different pore size distribution. However, when the method was used on corn stover, only differences in the accessible pore volume between unpretreated and pretreated corn stover can be detected. Only small differences were observed amongst the pretreated samples that gave ethanol yields ranging from 70 to 96%, and a poor correlation was found between the accessible volume and cellulose digestibility. NMR thermoporosity measurements were also unable to detect significant differences in the porosity of unpretreated and pretreated corn stover in the range of 20-200Å, even though this technique was more reproducible than the solute exclusion method.

Acknowledgement. The authors wish to thank the US DOE, Office of Biomass Programs, for funding this work.

References

(1) Grethlein, H. E.; Allen, D. C.; Converse, A. O. *Biotecnol. Bioeng.* **1984**, *26*, 1498.
(2) Grethlein, H. E. *Biotechnology* **1985**, *3*, 155.
(3) Stone, J. E.; Scallan, A. A. *Cellul.Chem. Technol.* **1968**, *2*, 343.
(4) Hansen, E. W.; Schmidt, R.; Stöcker, M. *J. Phys. Chem.* **1996**, *100*, 11396.

HIGH TEMPERATURE CONCENTRATED ACID HYDROLYSIS KINETICS OF PRETREATED PINE SAWDUST USING A CO-ROTATING TWIN-SCREW EXTRUDER

W. Scott Miller and Roger D. Hester

School of Polymers and High Performance Materials
The University of Southern Mississippi
Hattiesburg, MS 39406

Introduction

Very limited kinetic data exist on high-temperature concentrated acid hydrolysis of lignocellulosic materials. Most kinetic data published have been for lignocellulosic hydrolysis using dilute acid. In 1945 Saeman showed that the dilute acid saccharification of wood involves essentially two consecutive first-order reactions, cellulose to glucose and glucose to decomposition products[1].

Saeman was able to successfully model dilute acid hydrolysis of a number of wood species following this approach; however, he did make the observation that the experimental data indicated that there were in fact two reactions involved in the formation of glucose. The first, which was significantly faster than the second, was attributed to the "easily" hydrolysable fraction of cellulose. The second reaction involved the slower reaction of "difficult" to hydrolyze crystalline cellulose. The exact origin of the easy cellulose was not identified but was estimated to be roughly 10 % of the total theoretical glucose. Recent research has indicated that the origin of the easily hydrolysable cellulose is attributed to the amorphous regions of the cellulose[2]. The degree of amorphous regions available for hydrolysis within the cellulose can be significantly increased with pretreatment of the lignocellulosic material.

In 1985 Harris and co-workers published a more complete dilute acid model for cellulose hydrolysis[3]. This model contained reaction kinetics for seven different reactants and products: cellulose, glucose, levoglucosan, disaccharides, glucosides, and decomposition products. Most importantly, the cellulose was broken into two fractions, an easily hydrolysable fraction and difficult to hydrolyze cellulose fraction.

The Harris model assumed a 10 % easily hydrolysable fraction and achieved an excellent fit to experimental data. However, due to the assumptions made and the large number of differential equations used, it is difficult to determine with confidence, the magnitude of each rate constant. The purpose of this paper is to highlight a recent high-temperature, acid-hydrolysis kinetic study of southern yellow pine sawdust that was pretreated with concentrated acid using a co-rotating twin-screw extruder reactor (TSR).

Experimental

Sample Generation. The lignocellulosic material used was southern yellow pine sawdust, obtained from a particleboard plant located in the southeastern United States. Sieve shaker studies determined that the average sawdust size distribution was 4.5 % 40/45 mesh, 18.0 % 45/50 mesh, 17.1 % 50/60 mesh, 44.3 % 60/100 mesh, and 15.3 % 100 plus mesh. Following NREL laboratory analytical procedures it was determined that the material had an average moisture of 10 wt. % and composition of 34.3 wt. % cellulose on a dry sawdust basis[4].

Before high temperature acid hydrolysis the sawdust was pretreated by vibrationally feeding 4 g/min. of "wet" material into the TSR over one minute time intervals. The sawdust was then thoroughly mixed within the TSR with one part "wet" sawdust to 0.8 parts sulfuric acid. The acid was injected into the TSR as a 70 wt. % aqueous solution. The barrel temperature of the TSR was set at 60 °C. Orifices, having a 1/8" inside diameters, were placed at the exit of the TSR to achieve an average TSR exit pressure of 780 psi. The above TSR conditions were chosen from previous design-of-experiments approach that defined the capacity and strength limitations of the current equipment employed[5]. The pretreated lignocellulosic paste leaving the TSR had a Bingham type material rheology with a yield stress of 31,000 dyn/cm^2 and an apparent viscosity of 3,700 poise.

The extruder screws and barrel were fabricated at our machine shop from an acid resistant stainless steel alloy, AL6XN (Carpenter Technology Corp., Reading, Pennsylvania). Each 24-inch long screw had a 0.865 inch outside diameter with flights that produced a pitch of 0.438 inches. The trapezoidal flights had a tip width of 0.190 inches and a channel depth of 0.120 inches. The distance between screw centers was 0.75 inches. This design provided for complete screw intermeshing with an open passage between screws of about 30 %. The void volume within the 24 inch-long extruder available for material transport was 103 cm^3. Under the operating conditions used to generate the pretreated lignocellulosic material, roughly 79 % of the usable TSR void volume was filled with packed extrudate, producing about 10 minutes of material residence time within the TSR.

This amount of residence time allowed the sawdust to undergo significant particle size reduction and solubilization as a result of the high shear, high temperature, and high acid concentration environment. Upon exiting the TSR, 38.2 % of the dry sawdust solids were liquefied and capable of passing through a 15 micron filtering crucible. Of the 0.343 grams per dry gram of sawdust available for glucan production, 12.1 % was solubilized in the form of glucose. Application of NREL laboratory procedures showed that of the 38.2 % of dry sawdust solids that were liquefied, a total of 0.152 grams, or 44.2 % of the available glucan, was present in the form of glucose and soluble low molecular weight polysaccharides or oligomers.

Kinetic Analysis. The generated extrudate paste was mixed with water to achieve the acid concentration desired. The mixture was then placed in a custom fabricated 9.5" long zirconium reactor with an outside diameter of 0.50" and an interior diameter of 0.25". The reactor was sealed with threaded zirconium caps utilizing FETFE® O-Rings (Ace Glass, Vineland, NJ). The reactor was then placed in a heated oil bath for a specified time. Following the high temperature hydrolysis reaction the reactor was immediately placed in an ice bath for cooling. The resulting product was then diluted and prepared following NREL laboratory procedures for high pressure liquid chromatography (HPLC) compositional analysis[4].

Five different acid concentrations were prepared which ranged from 5 to 30 wt. % acid. These solutions were subjected to high temperature acid hydrolysis at 110, 120, and 130 °C with six time intervals collected at each combination of temperature and acid concentration. The experimental design resulted in seven unique sets of data having six data points each. Each experimental condition was replicated once.

Results and Discussion

To provide a more reliable model for our system, we have been able to achieve an analytically derived equation of glucose concentration as a function of time, acid concentration and temperature by incorporating the easy and difficult cellulose fractions into Saeman's model. The reaction scheme used is as follows:

where k_E is the easily hydrolysable cellulose fraction rate constant, k_0 is the difficult cellulose fraction rate constant and kg is the decomposition products rate constant.

Previous laboratory analysis of our pretreated TSR paste material indicated that the fraction of "easily" hydrolysable cellulose was much greater than 10 % of the theoretical total. NREL laboratory analyses indicated that roughly 44 % of the cellulose material exiting the TSR was in the form of glucose and solubilized low molecular weight polysaccharides which were capable of passing through a 15 micron filter. The fact that the material is solubilized indicates that at least 44 % must be easily hydrolysable. To take into account any other easily hydrolysable material that was not necessarily solubilized, we conducted the following analysis.

Research by Saeman and Harris et. al. has demonstrated that k_0 and kg are similar in magnitude and that k_E is much greater than both k_0 and kg. Following this assumption it can be said that nearly all glucose formed from cellulose in the early stages of a hydrolysis reaction results from the easily hydrolysable fraction. Thus, at the start of high temperature acid hydrolysis the following expression can be used as an approximation:

$$G \cong G_0 + E_0(1-\exp(-k_E t)) \qquad \text{Equation 1}$$

where G is the glucose concentration, G_0 is the initial glucose concentration, E_0 is the initial concentration of easily hydrolysable cellulose, k_E is the easily hydrolysable cellulose rate constant, and t is the time. In all expressions the concentrations are in moles/liter and the time is in minutes.

Using data collected at 110 °C and 7.82 wt. % acid hydrolysis conditions, it was then possible to do a nonlinear regression analysis of the first four data points to determine the two unknowns, E_0 and k_E, in Equation 1. From the two data sets, the resulting analysis yielded an average k_E and easily hydrolysable cellulose fraction, E_0, of 50 %. As expected, the fraction of easily hydrolysable cellulose was slightly higher than the amount of solubilized material (44 %) that had passed through the 15 micron filter.

The set of three differential equations representing the reaction of easily hydrolysable cellulose, difficult to hydrolyze cellulose and decomposition products can be simultaneously solved to give the following:

$$G = (k_E*E_0)/(kg - k_E)(1/(\exp(k_E*t)) - 1/(\exp(kg*t)))$$
$$+ (k_0*H_0)/(kg - k_0)(1/(\exp(k_0*t)) - 1/(\exp(kg*t)))$$
$$+ G_0/(\exp(kg*t)) \qquad \text{Equation 2}$$

where G is glucose concentration, k_0 is the difficult to hydrolyze cellulose rate constant, E_0 is the concentration of easily hydrolysable cellulose, kg is the rate constant of decomposition products formation, H_0 is the concentration of difficult to hydrolyze cellulose, G_0 is the initial concentration of glucose and t is the reaction time.

At the same hydrolysis condition used to determine E_0, Equation 2 has only two unknowns, k_0 and kg, because k_E has been determined. Using all of the glucose concentrations versus time data at 7.82 wt. % acid and 110 °C, nonlinear regression was used to find both k_0 and kg. Subsequent division of k_E by k_0 at each replication of the experimental condition produces an average multiplication factor of 50, i.e., $k_E = 50\ k_0$. This is the same relationship that Harris used in his research. Assuming that this relationship holds true at each hydrolysis condition, it is then possible to conduct nonlinear regression of Equation 2 to find k_0 and kg values at each of the remaining six reaction conditions.

Research conducted by Saeman used the following relationship for the dependence of a rate constant on acid concentration and temperature:

$$k = A(C_{acid})^B \exp(-E/RT) \qquad \text{Equation 3}$$

where k is a rate constant, A and B are constants, C_{acid} is the acid molar concentration, E is the activation energy in calories, R is the gas constant and T is the absolute temperature.

After transforming Equation 3 into logarithmic space, multiple linear regression was used to estimate k_0 and kg. This approach, as functions of temperature and acid concentration, produced the following reaction rate expressions:

$$k_0 = 4.779*10^7(C_{acid})^{1.032}(\exp(-18{,}180/(RT))) \qquad \text{Equation 4}$$

$$kg = 1.877*10^8(C_{acid})^{1.728}(\exp(-18{,}830/(RT))) \qquad \text{Equation 5}$$

where C_{acid} is the acid molar concentration, R is the gas constant, T is the absolute temperature, k_0 is the rate constant in minutes for the difficult to hydrolyze cellulose and kg is the rate constant in minutes for decomposition products. The rate constant for k_E is simply $50*k_0$.

Conclusions

Southern yellow pine sawdust is one of the most difficult lignocellulosic materials from which to extract the potential glucose present. Utilizing the TSR pretreatment technique it has been possible to obtain a significant quantity of glucose and low molecular weight polysaccharides, roughly 50 %, before high temperature acid hydrolysis begins. Application of the kinetic rate constants obtained from the static batch reactor hydrolysis studies described above demonstrates that more than 55 % of the theoretical glucose available in the pine sawdust can be obtained in a short reaction time, less than 20 minutes.

Application of this technology for the production of sugars for fermentation to ethanol shows great promise. However, from these studies it has been demonstrated that high glucose yields using short reaction times is dependent upon forming as much easily hydrolysable cellulose as possible in the pretreatment step. Future studies will explore continuous high-temperature, acid-hydrolysis kinetics and further optimization of the easily hydrolysable cellulose fraction obtained in the TSR pretreatment process.

Acknowledgement.

The authors wish to thank the Department of Energy EPSCoR program for funding, Derek Jacobs for laboratory assistance, and Jim Bridges and Steve Selph for TSR fabrication.

References

1. Saeman, J. F. *Industrial and Engineering Chemistry* **1945**, *37*, 43-52.
2. Ladisch, M. R. In *Biomass Handbook*; Kitani, O.; Hall, C., Eds.; Gordon and Breach Science Publishers: New York, 1989; pp 434-451.
3. Conner, A. H.; Wood, B. F.; Hill, C. G.; Harris, J. F. *Journal of Wood Chemistry and Technology* **1985**, *5*, 461-489.
4. Sluiter, A.; National Renewable Energy Laboratory, 2004; Vol. 2004.
5. Miller, W. S.; Hester, R. D. *Chemical Engineering Communications,* Submitted **2005**.

OPPORTUNITES FOR BIORENEWABLES IN OIL REFINERIES

T.L. Marker, J. Petri, T. Kalnes, M. McCall, D. Mackowiak
UOP LLC
28 East Algonquin Road
Des Plaines ,IL 60017

Doug Elliott
Pacific Northwest National Lab
902 Battelle Boulevard
Richland,WA 99352

Stefan Czernik
National Renewable Energy Laboratory
1617 Cole Blvd
Golden CO 80401

Prof David Shonnard
Michigan Technological University
1400 Townsend Drive
Houghton, MI 49931

Introduction

Although bio-fuel production has been expanding worldwide, so far there has been little integration with petroleum refineries. The segregation of bio-fuels increases the cost of bio-fuels use, since existing infrastructure for fuels distribution and production is not utilized. Bio-fuels could play a stronger role in reducing U.S. dependence on foreign oil if economical blending or coprocessing options could be developed in traditional oil refineries. This study identified some economically attractive opportunities for biofuel coprocessing, blending, and integration into typical oil refineries and defined areas where additional research is needed. A variety of biofuel feed types were evaluated as refinery feedstocks, including vegetable oils and greases, pyrolysis bio-oils and crude Fischer Tropsch liquids.

Key parts of the project included modeling, scoping experiments, cost estimates and economics. Economics were based on $40/bbl crude in a typical 150,000 bbl/d refinery, and sensitivities to higher crude prices of $50/bbl and $60/bbl were included. Life cycle analyses of key processes were compared, as well as opportunities for use of biorenewables to reduce refinery CO2 production.

Table 1. Costs of Biorenewable Feedstocks

Potential Bio Feedstock	$/bbl
Pyrolysis Oil	16
Crude Tall Oil	16
Brown Grease	21
Yellow Grease	40
Inedible Tallow	41
Jatropha Oil (India)	43
Palm Oil (Malaysia)	46
Soybean Oil	73
Rapeseed Oil	78

Experiments and Modeling

Properties of key feedstocks analyzed are shown in Table 2.

Table 2. Typical Properties of Biorenewables

	Crude	Resid	Soy oil	Yellow Grease	Pyrolysis Oil
%C	83-86	84.9	77.6	76.4	56.2
%H	11-14	10.6	11.7	11.6	6.6
%S	0-4	4.2	.0006	.04	-
%N	0-1	.3	.0011	.03	.3
%O	-	-	10.4	12.1	36.9
H/C	1.8-1.9	1.5	1.8	1.8	1.4
Density	.86avg	1.05	.92	.89	1.23
Tan #	<1	<1	2	30	78
ppm alkali metals	60	6	100	100	100
Heating Value BTU/lb	18,000	17,500	16,000	16,000	6560

The primary goal of the project was to look at economics of processing a variety of biorenewable feedstocks at petroleum refineries; only experiments that were needed to complete the economics were conducted. Proof of principle experiments were completed in:

1. cracking vegetable oils and grease in an FCC to make green gasoline and green olefins;
2. hydrotreating vegetable oil, grease and tall oil to make green diesel;
3. hydrocracking and FCC cracking of hydrotreated pyrolytic lignin to make gasoline;
4. blending pyrolysis oil and lignin with VGO and LCO.

Results and Discussion

When added to the FCC, vegetable oil readily cracks to make gasoline and olefins and makes less LCO and CSO when compared to a typical VGO feed. Green diesel, produced by hydrotreating vegetable oil and grease, can be made under typical diesel hydrotreating conditions from a variety of feedstocks, including high free fatty acid material. Green diesel requires no methanol feed and produces extremely high cetane material.

Pyrolytic lignin, which is the water insoluble fraction of pyrolysis oil, can be hydrotreated and cracked to make gasoline and diesel at conditions that minimize hydrogen requirements. The water soluble fraction of the pyrolysis oil can be reformed to make hydrogen; thereby, providing a biorenewable substitute for expensive natural gas typically used to make hydrogen in refineries.

The economics of various processing routes were compared for a variety of feedstocks. Vegetable oils and grease economics are shown in figures 1, 2, and 3. Subsidies are needed to allow rapeseed or soybean oil to become attractive, but low priced grease and tall oil can be economically processed without subsidies. As the price of crude increases, more options become economically attractive without subsidies.

LCA of green products were completed, which clearly show the environmental value of green diesel, green gasoline and biodiesel.

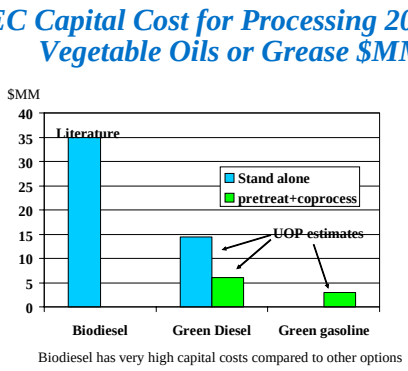


Figure 1. EEC Cost for Processing 2000 bpd of Vegetable Oil or Grease

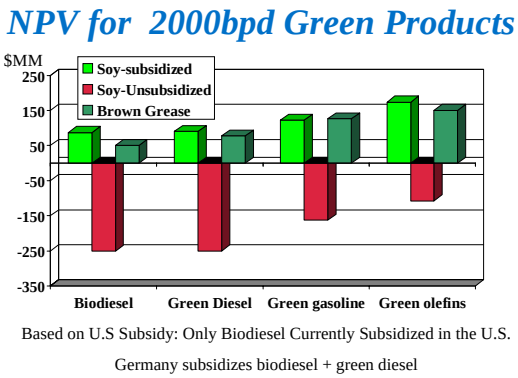


Figure 2. NPV for 2000 bpd of Green Products

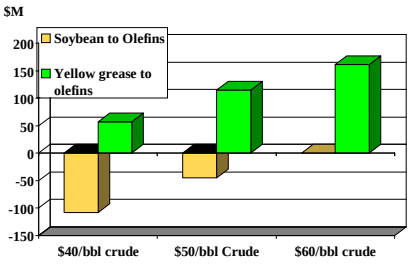


Figure 3. NPV Sensitivity to Crude price

Acknowledgment. This work was supported by the U.S. Department of Energy, the Office of the Biomass program.

PARALLEL PROCESSING BIOREFINERIES

Edwin S. Olson

Energy & Environmental Research Center
Box 9018
Grand Forks, ND 58202-9018

Issues in Agriculture-Based Feedstock Economies

Extensive development of an agriculture or biomass-based chemical industry is a long-term answer to both energy security and stimulation of rural communities in the United States. Two problems with production agriculture are the long-term excess productive capacity at acceptable prices and the widely fluctuating prices brought about by recent changes in federal farm program policy (1). The excess productive capacity problem could be alleviated by stimulating greater production of industrial products in biomass refineries. The biomass refinery, or "biorefinery," comprises biomass or agricultural processing facilities where raw products are converted via a chemical or biochemical process to high-value products and includes current plants, such as wet and dry mill ethanol plants, as well as more complex fiber and chemical industries, such as the new Blair, Nebraska, plant for production of dilactide and its conversion to polylactide and ethyl lactate. Currently, ethanol plants are being constructed, but it must be understood that government policy and fuel regulations are driving this operation. Many of the more complex plants will have the ability to utilize a variety of feedstocks and/or produce a greater variety of chemicals than the ethanol and lactide plants, which is very important in establishing a price-stable, market-driven industry, not one highly dependent on government subsidy and policy. As in a petroleum refinery, product flexibility allows profitability to be maximized by varying the product slate depending on current pricing, inventory, and demand. Thus the second problem of price fluctuation is solved by flexibility in the production at the refining level. And as in petroleum refining, ideally none of any feedstock will be wasted.

Parallel Processing Biorefinery (PPB) Concepts

Parallel processing of streams in a chemical plant can be an efficient way to produce a variety of materials. Parallel processing has always been an important feature of petroleum refining to achieve high efficiencies and allow flexibility in product selection. In contrast, biomass processing has been stuck on series processing. For example, grain or corn starch fermentation ends in ethanol with a low-value distillers grain by-product. Somewhat better is Blair lactate fermentation, which produces lactide polymer and an ethyl lactate by-product. In this case, the ethyl lactate is a way to utilize the racemic lactate by-product from the lactide separation tower. The process is parallel in the sense that two fermentations can be conducted on the same substrate to produce ethanol and lactate, and these two streams are then combined to produce ethyl lactate, but the fermentations may be conducted in different manners and using different equipment. This type of processing offers the potential for multiple parallel acid fermentations, producing a variety of acids that are combined with a variety of alcohols to produce many ester products. Ideally, the same equipment could be used in some or all of the parallel processes.

Opportunities in Biomass Feedstock Diversification or Flexibility

Today, about 99% of U.S. ethanol is made from the starch component of corn. Unlike the currently used starch feedstocks for the production of ethanol, such as corn, barley, and potatoes, or sucrose feedstocks, such as sugar cane, lignocellulosic feedstocks from fast-growing tree and grass crops and agricultural by-product or waste paper and other materials, are vast and cheap. For the parallel processing biorefinery, the diverse feedstocks should be converted to fermentable materials and/or a uniform chemical feedstock using the same equipment or process. This goal of flexibility in feedstocks is achievable with a thermal depolymerization process, such as the fast-pyrolysis technologies used in the Waterloo or Ensign processes, or acid pyrolysis in the levulinic acid processes. In fact, this flexibility may be the greatest advantage for fast pyrolysis over hydrolytic technologies.

The rationale for using pyrolysis to generate fermentable sugars from biomass is provided by recent technology performed by Ensyn Group, Inc., and earlier work performed by Weyerhauser Corporation, Crown Zellerbach, and the University of Waterloo in Ontario, Canada. The Weyerhauser work, which led to three U.S. patents, resulted in the development of a sawdust pyrolysis process for production of anhydroglucose at yields of about 25% of dry sawdust. Similar anhydroglucose yields were achieved by the University of Waterloo in pyrolysis of a variety of biomass feedstocks. Ensyn is currently operating two fast-pyrolysis units that have potential for producing an intermediate carbohydrate fraction for further processing.

The fast-pyrolysis process utilizes a low-pressure, high-flow-rate gas (steam, nitrogen, or a pyrolysis gas comprising carbon monoxide and carbon dioxide) to effect rapid removal of pyrolysis products from the heated zone, thereby preventing their destruction. The Ensyn process uses a hot sand bed to supply the energy for pyrolysis. Key products yielded from biomass pyrolysis include anhydrosugars, saccharinic acids, phenolics, furans, and smaller aliphatic aldehydes and carboxylic acids, which are derived from cellulose, hemicellulose, and lignin components of the biomass. Several anhydrosugars are present in the pyrolysis products, and most are not likely to be fermentable. However, the main anhydrosugar, levoglucosan, can be converted to glucose and fermented.

Given that greater product diversity will support the viability of biorefinery industries and consequently help sustain growth in rural economies, other pyrolysis products require further investigation to determine their potential for utilization in future fast-pyrolysis biorefinery concepts. There are several commercialized chemical transformations and uses of other pyrolysis products, and many more currently are under investigation. In addition to furans (2, 3) and other products described above, levoglucosenone has elicited considerable interest in the chemical community. Levoglucosenone (1,6-anhydro-3,4-dideoxy-α-D-*glycero*-hex-3-enopyranose-2-ulose) is formed during cellulose pyrolysis in phosphoric acid. This compound has potential importance as an intermediate for pharmaceutical syntheses (4 and references therein), owing to its chiral centers and functional groups (enone and acetal). Inexpensive sources of this intermediate are desired, as is further investigation of routes to chiral pharmaceuticals. Although several groups are exploring acid-catalyzed pyrolysis, it seems more practical to convert levoglucosan, available in large amounts from the fast-pyrolysis process, to levoglucosenone, since the levoglucosan is in fact an intermediate in the formation of levoglucosenone.

Opportunities in Parallel Fermentation Processes

The Energy & Environmental Research Center (EERC) recently proposed its concept of the dual-fermentation biorefinery (DFB) for efficient ester production (5–7). The DFB concept comprises the integration of ethanol production via yeast fermentation with the production of lactate via bacterial fermentation and the subsequent direct esterification of ethanol and ammonium lactate to produce high-value ethyl lactate. The key to the technical and economic

success of the DFB process is a highly efficient direct esterification that integrates the streams by facilitating the isolation and purification of the organic salt stream without extractions and membrane technologies. Using an ammonium salt concentrate avoids extractions and neutralizations needed in other processing schemes. Based on earlier U.S. Department of Agriculture patents for acid esterifications, EERC researchers developed (on the bench scale) an esterification process capable of extracting high yields of ethyl lactate from a 70% aqueous solution of ammonium lactate. Ammonia is recycled to the fermenter.

A PPB could also be configured with multiple fermentations to produce a variety of other ethanol-based carboxylate esters including ethyl acetate, propionate, butyrate, and succinate (6). These esters have high values as biodegradable low-toxicity solvents and chemical intermediates for the preparation of polymers and plasticizers, and several are potential high-octane gasoline additives with significant blending advantages versus ethanol. The PPB concept can potentially utilize a variety of biomass feedstocks, including starch hydrolysate, lignocellulose hydrolysate, hydrolyzed anhydrosugars from rapid pyrolysis, or pentoses from hemicellulose, and the separate fermentations may utilize different hydrolysates.

Another option for a PPB plant is to expand the variety of alcohols produced. This can be accomplished via the conversion of ethanol to n-propanol, isobutanol, n-butanol, and other higher alcohols (the Guerbet reaction). These have substantial markets as alcohols (solvents, fuel additives, chemical feedstocks) and can be used in esterification with the products from bacterial fermentation as previously discussed.

Commercialization of the PPB concept in any of the above configurations would provide ethanol plant product diversification options and enable revenue maximization through selective commodity production in response to changing market demands. In addition to providing diversified products for food, chemical, polymer, and fuel markets, the DFB concept is a unique opportunity for integrating recent and previous technical advances for processing carboxylic acids and their ester products.

References

1. Van Dyne, D.L.; Blase, M.G.; Clements, L.D. In *Perspectives on New Crops and New Uses* Janick, J., Ed.; ASHS Press: Alexandria, VA, 1999; p. 114.
2. Coutterez, C.; Gousse, C.; Gheneim, R.; Fang, S.W.; Gandin, A. In *Chemical and Materials from Renewable Resources;* Bozell, J.J., Ed.; Am. Chem. Soc.: 2001, p. 98.
3. Gravitis, J.; Vedernikov, N.; Zandersons, J.; Kokorevics, A. In *Chemical and Materials from Renewable Resources;* Bozell, J.J., Ed.; Am. Chem. Soc.: 2001, p. 110.
4. Witczak, Z.J. In *Chemical and Materials from Renewable Resources*; Bozell, J.J., Ed.; Am. Chem. Soc. 2001: p. 81.
5. Olson, E.S. U.S. Patent (provisional) Jan 2002.
6. Olson, E.S.; Aulich, T.R.; Sharma, R.K.; Timpe, R.C. Ester Fuels and Chemicals from Biomass. *Appl. Biochem Biotechnol*. **2003**, *105–108,* 843–851
7. Nagel, M.C. Biofuels, Technical Insights, Frost & Sullivan, Oct 2002.

REACTIVE DISTILLATION FOR THE BIOREFINERY: PRODUCTION OF ORGANIC ACID ESTERS

Navinchandra Asthana, Aspi Kolah, Dung Vu, Carl T. Lira & Dennis J. Miller

Department of Chemical Engineering & Material Science
Michigan State University
East Lansing, MI 48824

Introduction

The emerging development of the biorefinery concept for making fuels and chemicals from renewable biomass feedstocks has opened opportunities for novel reaction pathways and processes. Without doubt, the ultimate viability of the biorefinery lies in the successful development of these pathways and processes from economical and environmentally acceptable standpoint. While catalysis and new reaction pathways for biorenewables have received considerable attention over the past decade, separation processes for the biorefinery have lagged in their development.

Reactive distillation has been used extensively in the petrochemical industry to manufacture products such as methyl acetate and methyl tertbutyl ether. It is particularly effective when equilibrium reactions must be driven to completion; this is possible when one of the reaction products has volatility either greater than or less than the reactants.

In our laboratories, we have recently applied reactive distillation to the formation and recovery of several biorenewable chemicals. These applications include the recovery of propylene glycol and ethylene glycol from aqueous solution via reaction with acetaldehyde to form low-boiling acetals [1], transesterification of vegetable triglycerides and other organic esters for fuel and related applications, and formation of organic acid ethyl esters from their parent acids and ethanol. In this paper, we focus on organic acid ester formation using reactive distillation as a viable, low-cost route for production.

Reactive Distillation for Organic Acid Ester Production

The biorefinery concept is best visualized as an integrated facility involving both biological catalytic conversions (e.g. fermentation) and chemical catalytic conversions. Carbohydrate fermentations to ethanol and some organic acids are already mature, so that the platform species for organic acid ester formation are readily available and will continue to become lower in cost over time. Numerous applications for esters have been identified, including solvents, plasticizers, and fuels and fuel additives. In many cases, performance of the ester is superior to its petrochemical counterpart, but replacement has been limited by the higher cost of the ester. We present here a chemical catalytic approach using reactive distillation to form organic acid esters that will significantly lower the cost of their production and take full advantage of the existing biologically-based platform species.

We examine the formation of ethyl esters of lactic acid (a monobasic acid), succinic acid (dibasic) and citric acid (tribasic); these species have widely diverse physical and chemical properties but are already produced commercially via fermentation. The esters of these acids are desirable target species because of their attractive properties. Ethyl lactate and diethyl succinate are excellent solvents because they have low vapor pressures, very low toxicities, and excellent dissolving power. Tri-ethyl citrate has attractive plasticizer properties and low toxicity and is attracting attention in light of the toxicological hazards associated with using di-octyl phthalate as a plasticizer in children's toys. Beyond their desirable properties, these organic acid esters serve as prototypical compounds for the application of reactive distillation.

There have been a number of attempts to synthesize ethyl lactate in an efficient manner by utilizing lactic acid and ethanol [2-6]. While the chemistry involved in lactic acid esterification with ethanol is very simple, obtaining purified ethyl lactate in high yield is difficult because of the equilibrium limitation resulting from the presence of water. Further, ethyl lactate formation is further complicated by the tendency of lactic acid to polymerize in solution to linear dimer and higher esters, particularly as water is removed. Thus, good yields are difficult to achieve via conventional means, resulting in a relatively high selling price (>$3.00/kg) for the ester.

Reactive distillation circumvents these difficulties by driving the reaction to completion via water removal during reaction. Because of this, a high purity product stream is produced that contains only ethyl lactate and lactate oligomer esters. The oligomer esters are easily separated from ethyl lactate and can either be used as co-products (e.g. for plasticizers, etc.) or further reacted to increase the yield of ethyl lactate to near its theoretical limit.

Diethyl succinate is currently produced either from maleic anhydride via dimethyl maleate transesterification and hydrogenation, or by direct esterification of succinic acid with ethanol in multiple reaction-distillation steps. Triethyl citrate is synthesized using pure citric acid and ethanol. Since both acids are polybasic, the extent of reaction to final product is rate limited as well as equilibrium limited. They thus pose good opportunities for the application of reactive distillation.

Experimental Methods

Reagents. Aqueous lactic acid solution containing 88 wt% was obtained from J. T. Baker. Absolute ethanol (99% purity) and HPLC grade water were procured from J.T. Baker. Ethyl lactate was procured from Acros Organics. Succinic acid, citric acid, monoethyl succinate, diethyl succinate and triethyl citrate were procured from Sigma-Aldrich. All chemicals were used as received for reactive distillation experiments.

Reactive distillation. Lactic acid esterification reactions were performed in a pilot-scale reactive distillation column with a height of 5.5 m and an inside diameter of 0.05 m., packed with Sulzer Katapak structured packings containing Amberlyst 15 ion exchange resin [1]. The column is equipped with feed pumps, ports to remove samples and monitor column temperature, a reflux splitter, and a reboiler with overflow for level control. The entire column is wrapped in heating tape and insulated to minimize heat loss. In continuous operation for esterification, aqueous lactic acid solution is fed near the top of rectifying zone, 4.5 m above the reboiler, while ethanol is fed near the bottom of the stripping section, 0.09 m above from the reboiler.. Typically, the column takes about six hours to come to steady state. Samples are collected from the distillate and bottoms streams for product analysis at steady state. Material balances were conducted for each run to characterize column performance and quantify product distribution.

Batch esterification. Batch esterification reactions were performed in an 80 mL glass reactor equipped with a water condenser, sample port, thermocouple and an outer heating oil jacket for isothermal operation at elevated temperature. Samples were drawn periodically for analysis.

Analysis. Ethanol and water from all samples were analyzed by gas chromatography (Varian 3600; TCD with He as a carrier gas) using two different stainless steel column (3.25 mm X 4 m) packed with a liquid stationary phase of Porapak-Q. Lactic acid, its oligomers, succinic acid, citric acid, and their respective esters were quantitatively analyzed by HPLC using a reverse-phase C18 column with water and acetonitrile as mobile phase, and with UV detector set

at a wavelength of 210 nm. Compounds were identified by comparing their retention times with known standards.

Results and Discussion

Lactic acid esterification via reactive distillation. In optimized operation, water and ethanol constitute the distillate stream from the column and the bottoms stream contains only ethyl lactate and lactate oligomer esters. Fig. 1 delineates the effect of ethanol mole ratio on lactic acid conversion and desired product purity. Reducing the mole ratio of ethanol from 3.6 to 1.4 had little effect on acid conversion, but formation of L_2E and higher oligomer esters increased. The molar yield of L_1E decreased with decreasing mole ratio because of a lower concentration of ethanol in the reactive zone, but a lower ethanol feed rate also resulted in less ethanol and water in the bottoms stream and thus a higher purity ester product (open squares in Fig. 1).

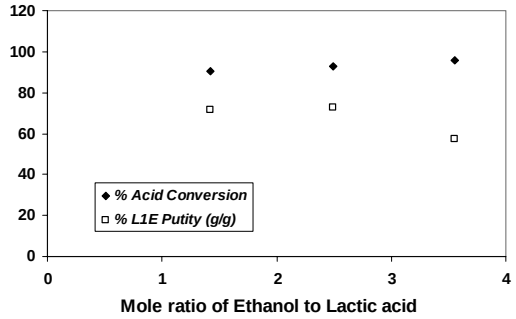


Figure 1. Effect of Mole Ratio of ethanol to lactic acid. Lactic acid and ethanol feed temp.: 25°C; Reflux ratio: 0

Fig.2 shows the effect of reflux ratio on acid conversion and bottoms product purity. Lactic acid conversion and bottoms product purity were both adversely affected by increasing reflux ratio – this is because reflux contains significant water which causes ester hydrolysis. The best mode of operation is therefore with no reflux, making the column operate as a reactive stripping column.

Increasing ethanol feed temperature from 25°C to 78°C (saturated liquid feed) and up to 85°C (vapour feed) has a deleterious effect on lactic acid conversion and L_1E yield, although water and ethanol are removed from the bottoms stream of the column and thus better product purity is observed (Fig 3).

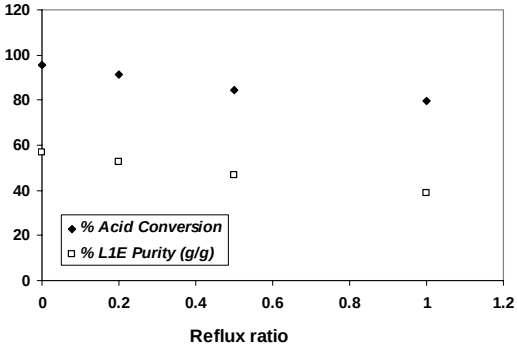


Figure 2. Effect of Reflux Ratio. Ethanol to lactic acid molar ratio 3.6 : 1; Lactic acid and ethanol feed temp.: 25°C

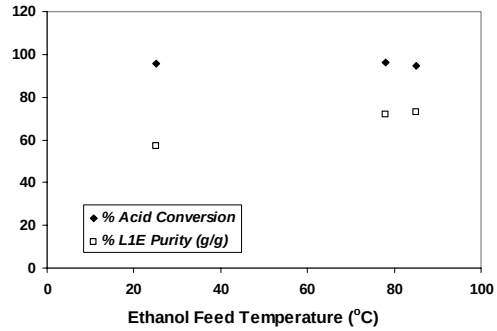


Figure 3. Effect of Ethanol feed temp. Ethanol to lactic acid molar ratio 3.6 : 1; Lactic acid feed temp.: 25°C; Reflux ratio : 0

Succinic acid and Citric acid esterification. Batch esterification reactions for succinic acid (SA in Table 1) and citric acid (CA) were conducted with molar ratio of ethanol to succinic acid and citric acid of 10 and 15, respectively. The reactions were catalyzed by Amberlyst 15 cationic exchange resin as catalyst (5 w/w solution).

Esterification takes place via sequential conversion of –COOH groups in acids. The rate of esterification of the first –COOH group is fast, but subsequent esterification rates are relatively slower and are highly dependent on temperature. Results in Table 1 are at 1 hr.

Table 1. Batch esterification of citric and succinic acids

T (°C)	SA Conv (%)	% Selectivity		CA conv (%)	% Selectivity		
		Mono ES	Di ES		Mono EC	Di EC	Tri EC
80	77.3	63.5	36.4	29.3	87.2	12.3	0.4
90	88.6	49.4	50.5	59	70.4	26.1	3.4
100	92.5	40.4	59.5	76.9	53.3	37.1	9.4
110	95.6	26.7	73.2	87.4	43.6	43.8	12.4

Conclusions

We have shown that ethyl lactate can be synthesised from aqueous lactic acid solution in high purity using reactive distillation. Ethyl esters of succinic and citric acids can be synthesized in high yield using various reactor configurations at high temperature.

Acknowledgement. Financial support from the National Corn Growers Association and U.S. Department of Energy are greatly appreciated.

References

[1] Dhale A. D., Myrant L. K., Chopade S. P., Jackson J. E., Miller D. J. *Chem. Eng. Sci.*, **2004**, *59*, 2881-2890.

[2] Cockrem M. C. M. "Processes for Production of Esters", *US 6664413*, 2003.

[3] Kaimal T. N. B., Vijayalaxmi P., Ramalinga B., Laxmi A. A., "Process for Preparation of Alkyl Esters From Commercial Lactic acid", *US 6342626*, 2002

[4] Datta R., Tsai S-Perng, "Esterificaiton of Fermentation-Derived Acids via Pervaporation" US 5723639, 1998.

[5] Jafar J. J., Budd P. M. & Hughes R., *Journal of Membrane Science*, **2002**, *199*, 117-123.

[6] Tanaka K., Yoshikawa R., Ying C., Kita H.& Okamoto K., *Chem. Engg. Sci*, **2002**, *57*, 1577-1584.

CONVERSION OF BIOMASS RESIDUES TO TRANSPORTATION FUELS WITH THE HTU® PROCESS

J. E. NABER and F. GOUDRIAAN, J.A. ZEEVALKINK

Biofuel B.V.; Rendorppark 30, 1963 AM Heemskerk, The Netherlands, TNO-MEP; Postbox 342, 7300 Apeldoorn, The Netherlands

Introduction

The uniquely innovative HTU® process for the thermochemical liquefaction of biomass offers excellent opportunities for conversion of biomass to a transportable form of energy. Suitable feedstocks include residues from agriculture and forestry, and also peat. Biomass is quantitatively and efficiently converted by treatment in liquid water at temperatures from 300 to 350°C and pressures from 100 to 180 bar. The product is 'Biocrude', a heavy organic liquid with 10-15%w oxygen and a heating value of 30-35 MJ/kg. It readily separates from water. Due to the low oxygen content it can be further upgraded cost-effectively by hydrodeoxygenation to a clean diesel-type fuel with high cetane number, that offers excellent prospects for direct blending with existing (conventional) automotive diesel fuels.

The development of the HTU® Process has now reached a stage that a follow-up with commercial demonstration can be undertaken. Based on the results of the R&D, the conceptual designs have been concluded with a basic design package. Subsequently, a technical and economic feasibility study for a first commercial demonstration plant showed excellent perspectives. The results confirmed that the HTU® process is well placed technically and economically, with an excellent potential for upscaling and rapid rate of commercial development.

An international consortium has been formed and preparations are now being made for the design and construction of the first commercial demonstration of the HTU® process at a scale of 25,000 tons biomass (dry basis)/year. The HTU®-1 unit is planned for start-up in 2008 at a location next to the Waste Burning Facility of the Afval Energie Bedrijf AEB (Waste Processing Agency) of the City of Amsterdam.

Based on the products from HTU®-1, a parallel programme has been developed for the demonstration of HTU®-diesel. This programme includes

- Hydrodeoxygenation of some 30 tons of light biocrude
- Assessment of diesel quality and formulation of additives package
- Engine testing and monitoring of field test with 3-5 trucks/buses
- Commercial distribution and logistics

At least two follow-up commercial units of each 200,000 tons biomass throughput (dry basis)/year at the same location (start-up in 2011) and nearby, will allow the commercial introduction of HTU®-diesel.

Key points for the further commercial development are:

- HTU® is a cost-effective route from (wet) biomass rest products into automotive diesel.
- Final products are fully compatible with traditional transport fuels
- Fuels can be used in existing engines and no separate distribution system is required
- The HTU® route further opens perspective for production of 'green' chemicals in existing chemical installations

CARBONIZATION OF CELLULOSE UNDER MECHANICAL PRESSURE AS A MEANS FOR INCREASING CHAR YIELD

Kouichi Miura, Hiroyuki Nakagawa,Ryuichi Ashida, Yuji Sakuramoto, and Kyosuke Nakagawa[*]

Department of Chemical Engineering, Kyoto University, Kyoto-Daigaku Katsura, Nishikyo, Kyoto 615-8510, JAPAN

Introduction

We have recently presented a new method that produces high strength granular activated carbons from biomass wastes without any binders[1)]. A sawdust, a bamboo, a recycling paper, and a newsprint paper were employed as the raw materials. The samples were pre-carbonized under the mechanical pressure of around 10 MPa at the temperature range of 25 °C to around 300 °C, called hot press carbonization in this work, to prepare densified semi-chars. The semi-chars were subsequently carbonized and activated to prepare high strength activated carbons. The hot press carbonization surprisingly increased the char yield by 1.9, 4, and 5 times for the sawdust, the recycling paper, and the newsprint paper, respectively. The strength of the activated carbons was dramatically increased by the hot press carbonization. The BET surface area of the activated carbons produced from the sawdust and the recycling paper reached as large as 1000 m^2/g. It was found that cellulose in the biomass wastes played a crucial role to increase the char yield and to develop pore structures.

In this paper the mechanism of pyrolysis of cellulose under mechanical pressure was examined in detail to clarify the mechanism by which the char yield increased.

Experimental

A cellulose microcrystalline (MERCK) was used as a cellulose (Elemental composition on daf basis; C: 44.1 %, H: 5.7 %, N: 0.3 %, O: 49.9 %).

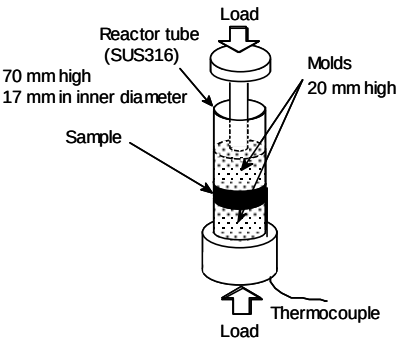


Figure. 1. Schematic of reactor used for hot press semi-carbonization.

Carbonization of the cellulose was performed in two steps: the first step is semi-carbonization below 300 °C to prepare semi-char and the second step is carbonization of the semi-char in a nitrogen atmosphere up to 900°C under atmospheric pressure to prepare char. The semi-carbonization under 10 MPa of mechanical pressure, which is called "hot press semi-carbonization", was performed using the reactor shown in Fig.1. About 2 g of sample were placed between the molds, heated radiationally by a so-called infrared-image furnace (Shinku-Riko, RHL-P610P) at the rate of 10 K/min to 300°C, where they were maintained for 15 min. Three other experimental conditions were employed for the semi-carbonization for comparison purpose. Their abbreviation and experimental detail are as follows:

Normal semi-carbonization: Heat treated like hot press semi-carbonization, but without the mechanical pressure and the upper mold.

Low temp. semi-carbonization: Heat treated at 260°C for 20 h without the mechanical pressure and the upper mold.

Gas pressure semi-carbonization: About 1 g of sample embedded in a tubing-bomb reactor under 1 MPa of nitrogen were heated at 10 K/min to 300°C at which they were maintained for 15 min. The pressure finally increased up to 6.5 MPa.

The second step carbonization was performed using a thermobalance in which about 2mg of semi-char were heated at 10 K/min to 900°C. Semi-chars and chars prepared were characterized by various analytical methods.

Results and Discussion

Semi-carbonization. Figure 2 shows the yields of semi-chars prepared under the four different conditions. The yields were significantly different, depending on the experimental conditions. The largest yield of 0.82 was obtained under normal semi-carbonization. Both gaseouos and mechanical pressures accelerated the semi-carbonization to decrease the semi-char yields down to

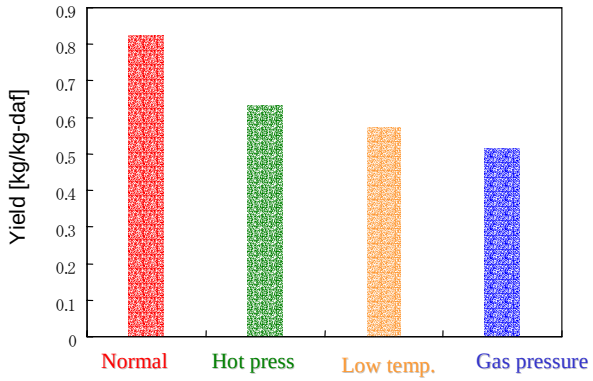


Figure 2. Yields of semi-chars obtained by different semi-carbonization conditions.

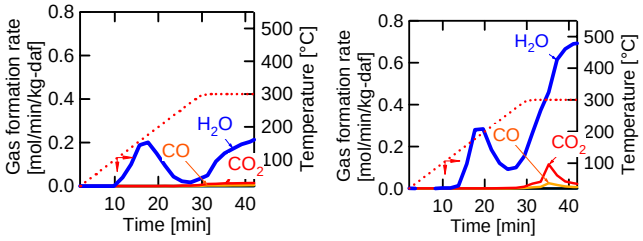


Figure 3. Gas formation rates during semi-carbonization. Left : normal semi-carbonization, right: hot press semi-carbonization.

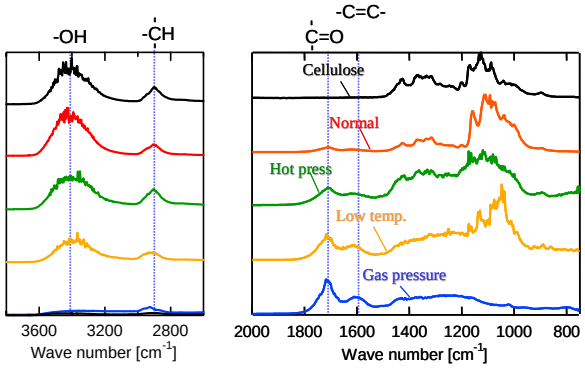


Figure 4. F.T.i.r. spectrum of the semi-chars obtained by four semi-carbonization conditions.

0.52 and 0.63, respectively. Low temp. semi-carbonization also decreased the semi-char yield down to 0.57.

Figure 3 compares gas formation rates during semi-carbonization between normal semi-carbonization and hot press semi-carbonization. The formation rates of the main gaseous product H_2O were significantly different between the two semi-carbonization methods, and the yields were 0.06 and 0.25 for normal semi-carbonization and hot press semi-carbonization, respectively. On the other hand, the tar yields were 0.12 and 0.03 for normal semi-carbonization and hot press semi-carbonization, respectively.

The overall stoichiometry of the semi-carbonization was formulated from mass balance as follows:

Normal semi-carbonization:

$$(C_6H_{10}O_5)_n \rightarrow 0.54nH_2O + 0.13(C_6H_{8.9}O_{4.3})_n + 0.87(C_6H_{8.9}O_{4.5})_n$$

Cellulose Tar Semi-char

Hot press semi-carbonization:

$$(C_6H_{10}O_5)_n \rightarrow 0.11nCO_2+2.33nH_2O+0.09(C_6)_n + 0.90(C_6H_{6.2}O_{2.7})_n$$

Cellulose Tar Semi-char

Figure 4 compares the F.T.i.r. spectra of the semi-chars prepared under four different conditions with the spectrum of the cellulose. It is clear that the semi-char prepared by normal semi-carbonization conditions retain the structure of the cellulose. On the other hand, the semi-chars prepared by other three conditions had distinct peaks attributed to >C=O, and the semi-char prepared by gas pressure semi-carbonization had lost the peaks attributed to –OH. These results show that the mechanical pressure accelerated the crosslinking reactions of –OH group, resulting in acceleration of gaseous components but suppression of the formation of tar. Similar effects appeared by both gas pressure semi-carbonization and low temp. semi-carbonization. The chemical compositions of tar and the semi-char produced by normal semi-carbonization were rather close to the composition of the cellulose, but they were significantly different from the composition of the cellulose for hot press semi-carbonization and were rich in carbon.

Carbonization. Figure 5 shows the weight changes during the carbonization for the semi-chars prepared under four different conditions. The ordinate of Fig. 4 represents the yield relative to the original cellulose. The yield at 900 °C was only 0.07 for the semi-char prepared under normal semi-carbonization, whereas the yields were, 0,27, 0.25, and 0.20 for the semi-chars prepared under hot press semi-carbonization, gas pressure semi-carbonization, and low temp. semi-carbonization, respectively.

Figure 6 compares the formation rates of gaseous products and tar between the semi-chars prepared by normal semi-carbonization and hot press semi-carbonization. Most significant difference between the two semi-chars is the tar formation behavior. For the semi-char prepared by normal semi-carbonization, a large tar formation peak appeared at around 350 °C, which accounted for more than 90 % of weight decrease (0.60 kg/kg-cellulose) during the carbonization. Furthermore, the chemical composition of the tar was rather close to that of the cellulose. On the other hand, the amount of tar formed was only 0.16 kg/kg-cellulose for the semi-char prepared by hot press semi-carbonization, and the chemical composition of the tar was rich in carbon and is significantly different from that of the cellulose. This difference in the tar formation behavior is reflected to the difference in the H_2 formation rates at higher temperature region. A large H_2 formation peak at around 760 °C for the semi-char prepared by hot press semi-carbonization is judged to come from aromatic ring condensation reactions of the char precursors retained due to the suppression of tar formation.

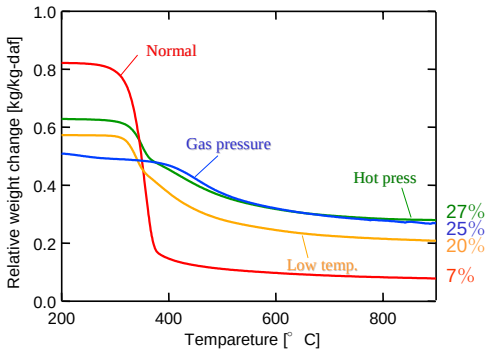
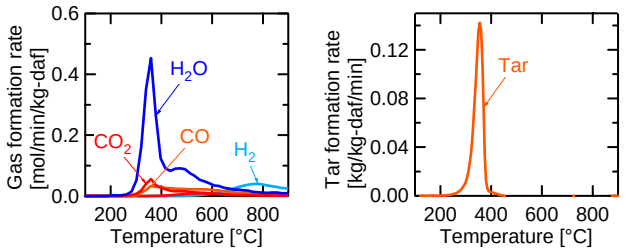
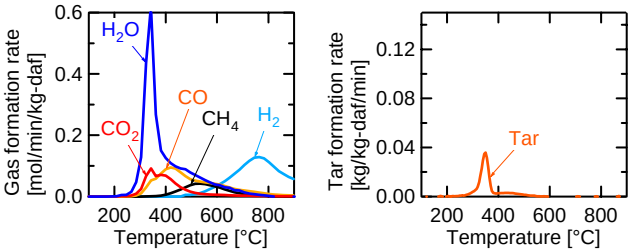


Figure 5. Weight changes during carbonization of the semi-chars prepared by four semi-carbonization conditions.



(a) Semi-char prepared by normal semi-carbonization.



(b) Semi-char prepared by hot press semi-carbonization.

Figure 6. Gas and tar formation rates during carbonization of the semi-chars.

Conclusion

It was clarified that the final char yield of the cellulose is significantly affected by the dehydration reaction that proceeds rather slowly at around 250 to 300 °C under atmospheric pressure. The dehydration reaction can be accelerated by either hot press carbonization or gas pressure carbonization. Both mechanical pressure and gaseous pressure suppresses the evolution of tar components, which enhances the dehydration reactions among the tar components. Therefore, both mechanical pressure and gaseous pressure are judged to be effective to increase the char yield through the carbonization of biomass. However, only mechanical pressure can increase the strength of the char as well, which will be very advantageous when preparing high performance carbon materials from biomass.

References

(1) Miura, K; Nakagawa, H.; Ashida, R.; and Nakagawa, K. *Carbon 2003* (Oviedo, Spain), Abs. No. 177.

PRODUCTION OF BIO-CARBON ADSORBENTS FROM FOREST THINNING

Eun-Jae Shin[1], *Robert J. Evans*[1,2] *and Andrew M. Herring*[1]

[1]Department of Chemical Engineering, Colorado School of Mines, Golden, CO 80401, USA
[2]Electric & Hydrogen Technologies & System, National Renewable Energy Laboratory, Golden, CO 80401, USA
Tel: 303-384-2046, Fax: 303-274-3730
E-mail: eshin@mines.edu

Introduction

Large portions of the forested land contained in the US are at extreme risk of wild fire. It is, therefore, proposed to treat the forest to reduce the risk of catastrophic fires. The two most effective methods of forest treatment are mechanical thinning and prescribed burning or a combination of the two. There is, however, no economic incentive and there are still significant risks of sparking catastrophic wildfire and degrading air quality through the production of CO and particulate matter (PM) [1]. There is growing interest in converting forest slash to value-added fuels and chemicals. This has advantages that such value-added products reduce the nation's dependence on imported fossil fuels and, if a forest is harvested in a sustainable manner, a significant contribution is also made to the reduction of CO_2 emissions and so reduces climate changes [2].

Leadville, Colorado is surrounded by a large, fire-prone Lodgepole Pine forest, which means that a wood resource is available for the development of bio-carbons. Leadville also sits on a superfund site that was left behind by past mining activities. The impact on Colorado water resource is significant and protection of water by active and passive systems is important.

The objective of this work is to develop bio-carbon adsorbents from forest thinnings and apply them locally to the protection of natural waterways from acid mine drainage (AMD).

Experimental

Production of Char and Activation of Carbon. We made wood cubes out of fresh cut Lodgepole Pine with different sizes, i.e., 3mm, 6mm and 12mm. Sawdust and bark were also used to study the effect of sample sizes as well as sample materials. Variation in locations where the feedstock was from was also considered: (Location 1: ≅13 yrs), Location 2 (≅18 yrs) and Location 3 (≅ 25 yrs). We used the tree from Location 1 throughout the work if it is otherwise specified. We have used a quartz tubular reactor heated by an electric furnace to vacuum pyrolyze the biomass at moderate temperatures. The samples were charred at a pressure of 20 kPa over temperature range from 400ºC to 500ºC for 1hr. Chars obtained by vacuum pyrolysis have been found to be more reactive in the activation process, compared to those obtained by atmospheric carbonization [3]. Pretreatment of feedstock with phosphoric acid was also applied prior to charring. 5% of phosphoric acid solution was used to be penetrated through the sample overnight and the soaked samples were air dried at room temperature: weight percent of phosphoric acid to the sample was 1%. 20g of each sample were placed in the tubular reactor and heated to a desired temperature. 20 kPa pressure was obtained by using a water aspirator and the vacuum pyrolysis run time was 1 hr. Temperatures were varied from 400°C to 500°C.

Char was activated at 700°C with steam for 1hr in the same reactor under atmospheric pressure. Ar (>99% pure) was introduced to the reactor until it reached the temperature and it was switched to steam of 5 g/hr. After 1hr, Ar gas was again introduced to the reactor to cool it to room temperature.

Characterization of Char and Carbon. The chars and carbons were characterized primarily with BET surface area, Iodine (ID) number, DRIFTS, TGA and ESEM. BET surface area was measured with Micrometritics Flowsorb II 2300. All samples were subject to degassing for 2 hrs in He at 150°C before surface area measurements. Iodine (ID) numbers were also measured following a modification of test method ASTM D4607-86 [4].

For the DRIFTS experiments, the samples were ground in air and placed in Harrick Scientific, heatable variable atmosphere chamber in a Harrick Scientific Praying Mantis Diffuse Reflectance attachment. The DRIFTS was recorded at room temperature using Thermo-Nicolet Nexus 760 FT-IR spectrometer. TGA analysis was performed using a Seiko TGA balance, sample size about 2 mg at a heating rate of 10 °C/min from ambient to 700°C. Scanning Electron Microscope (SEM) images were taken by using FEI Quanta 600 with 100 magnification.

Results and Discussion

Characteristics of Chars. The yields of chars were about 25% of initial weight of wood that were pyrolysed at 400°C. At 500°C, the yield was lowered to 20%. For chemically pretreated samples, the char yield was about 35% and this high char yields could be explained with lower temperature crosslinking reactions that led to retention and incorporation of dehydration products and volatiles [5].

BET surface areas (SA) of chars obtained with non-pretreated samples are listed in the Table 1 where char yields and ID numbers are also included. ID numbers indicates the porosity of the chars and represents the surface area contributed by the pores larger than 10 Å [6]. To verify our approach to measure ID number, we tested it with a commercial activated carbon and the result is shown in Table 1. Based on the manufacturer's information (Fisher Scientific), our method was validated.

It is obvious that smaller sized samples resulted in higher surface areas. While 3mm cubes yielded highest surface area among the samples, that of sawdust was not as high as expected due to its small particle sizes. It can be attributed to less porous sites that sawdust might have, which coincides with lower ID number for sawdust, compared to that of 3mm cubes. Location also affected the results.

Table 1. Physical Characteristics of Chars generated at 400°C and 20 kPa pressure.

Wood Sample	Yield (%)	BET SA (m^2/g)	ID No. (mg/g)
Location 1			
3mm Char	21	270	161
6mm Char	24.8	170	-
12 mm Char	23.5	120	27
Sawdust	25.2	130	70
Bark	24.2	130	110
Location 2			
3mm Char	22	350	-
Location 3			
3mm Char	24.5	400	-
AC (Fisher)	-	1150*	992

*The manufacturer's information

For the char produced with 3mm cubes of Lodgepole Pine at 500°C, BET surface area was 120 m^2/g, which is lower than that of the char produced at 400°C. It can be rationalized with possible secondary reactions of the volatiles at higher temperatures, which

could lead to condensation on the surface.

The DRIFTS of the chars are shown in Fig. 1 where it can be observed that the band of aliphatic C-H bond at 2900 cm^{-1} is more abundant for bigger sample sized samples (6mm and 12mm) and bark. For all samples, there are lignin-like structures still remained.

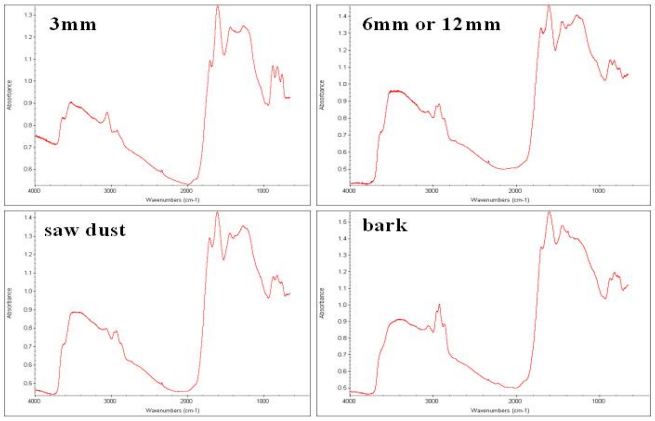


Figure 1. DRIFTS of the chars produced with Lodgepole Pine at 400°C and 20 kPa pressure.

TGA data for the chars is shown in Fig. 2. The weight loss of 3mm cubes was less than other samples, indicating that this char is by most stable.

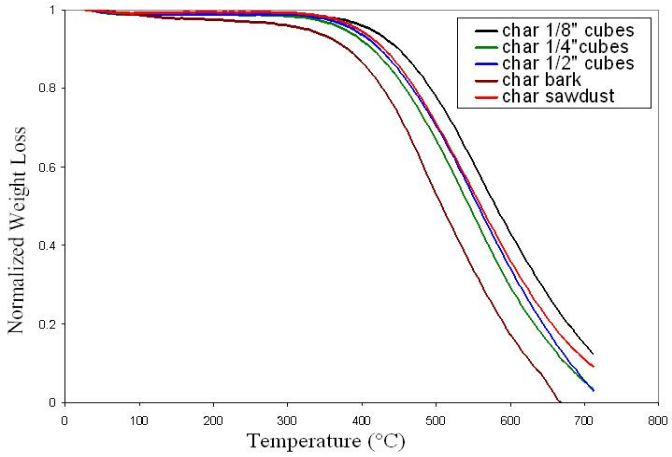


Figure 2. TGA for the chars produced with Lodgepole Pine at 400°C and 20 kPa pressure.

SEM images reveal morphology of a wood cube and its char as shown in Fig. 3 where it is obvious that porous sites were heavily developed by carbonization through removing volatiles.

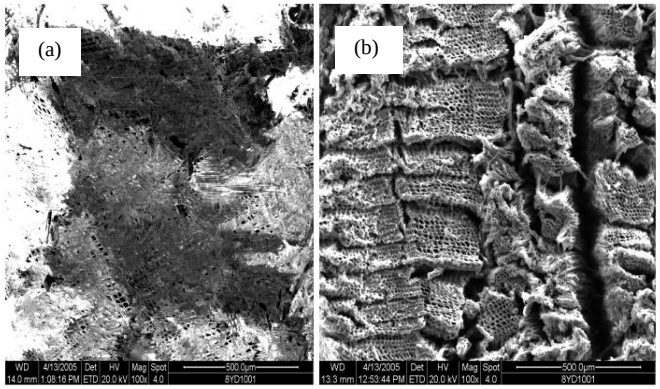


Figure 3. SEM images of (a) 3 mm Lodgepole Pine cube and (b) its char produced at 400°C and 20 kPa pressure.

Figure 4 shows porous sites of the chars produced without and with the pretreatment. More open pores are observed with the char obtained with the pretreated sample (Fig. 4 (b)).

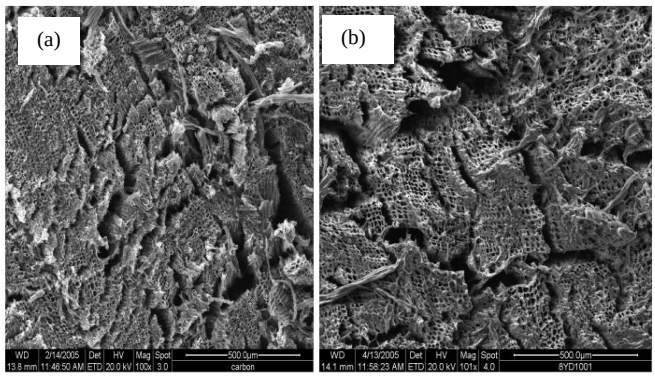


Figure 4. SEM images of the chars produced with Lodgepole Pine charred 12 mm cubes at 400°C and 20 kPa pressure: (a) non-pretreated and (b) 1% phosphoric acid pretreated sample.

BET surface area measured for the two chars in Fig. 4 (a) and (b) were 120 m^2/g and 400 m^2/g, respectively, which might be resulted from dehydration induced by the acid. Shafizadeh reported increased water yield from 11% to 21% during the pyrolysis of cellulose treated with 5% H_3PO_4 [7].

Characteristics of Activated Carbons. Carbon yields were about 50% and those of pretreated samples were about 70%. This can be again due to crosslinking induced by the acid [4].

The chars of non-pretreated sawdust and 3mm cubes, produced by vacuum pyrolysis were selectively activated and their BET surface areas were measured. The results were 750 m^2/g and 1000 m^2/g for sawdust and 3mm cubes, respectively.

The toxicological test for the carbons is under the way. In addition, the tests for the capability of the carbons as adsorbents for metal adsorption are in progress.

Conclusions

Our preliminary data have showed that by using vacuum pyrolysis at the moderate temperature followed by steam activation, it is possible to obtain high quality carbons that are comparable to commercial carbons, e.g. comparable BET surface areas. Moreover, when feedstock is pretreated with chemical reagents such as phosphoric acid, the quality of carbons can be even more improved.

With further study, we should be able to develop cost-effective activated carbons produced from local carbon sources, such as tree thinnings, for the protection of natural waterways from AMD.

Acknowledgment. The authors thank Alex Lauve, Jim Martineau and Sarah Stokes for their experimental assistance. This work was supported by the Division of Education and Research, Colorado Institute of Technology.

References

(1) MacNeil, .J.S. *Science*, **2000**, 289, 1448b.
(2) Kadam, K.L.; Wooley, R.J.; Aden, A.; Nguyen, Q.A.; Yancey, M.A.; Ferraro, F.M. *Biotechnol Prog*., **2000**, *16*, 947.
(3) Cao, N.; Darmstadt, H.; Roy, C. *Energy & Fuel*, **2001**, *15*, 1263.
(4) Matsumura, Y.; Xu, X.; Antal, M.J. Jr. *Carbon*, **1997**, *35*, 819.
(5) Solum, M.S.; Pugmire, R.J.; Jogtoyen, M.; Derbyshire, F. *Carbon*, **1995**, 33, 1247.
(6) Srinvasakanna, C.; Bakar, M.Z.A. *Biomass and Bioenergy*, **2004**, *27*, 89.
(7) Shafizadeh, F.; Chin, P.S. ACS Symposium series, **1977**, *43*, 57.

NEW SOLID BASES FOR BIODIESEL SYNTHESIS

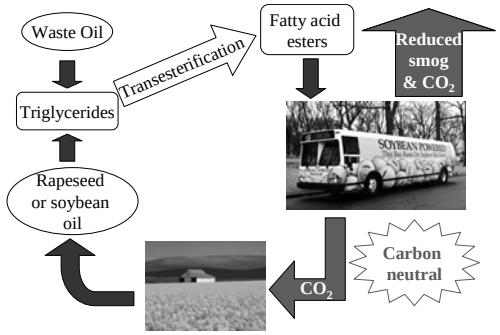
Karen Wilson[*]*, David G. Cantrell, Lisa J. Gillie*[2]*, Robert S. Watkins and Adam F.Lee*

University of York, Department of Chemistry, York, YO10 5DD, United Kingdom.

[2]University of Sheffield, Department of Engineering Materials, Sheffield, S1 3JD, United Kingdom.

Introduction

Fatty acid esters are widely used in the synthesis of lubricants, oleochemicals, surfactants, polymers and more recently biodiesel[1]. Biodiesel is a promising nontoxic and biodegradable renewable fuel comprised of mono-alkyl esters of long chain fatty acids, which are derived from vegetable oils or animal fats. Biodiesel is oxygenated and essentially free of sulfur making it a cleaner burning fuel than petroleum diesel with reduced emissions of SO_x, CO, unburnt hydrocarbons and particulate matter[2]. Biofuels are also carbon neutral as CO_2 emitted from the vehicle is consumed during photosynthesis by the crops as illustrated in **scheme 1**.

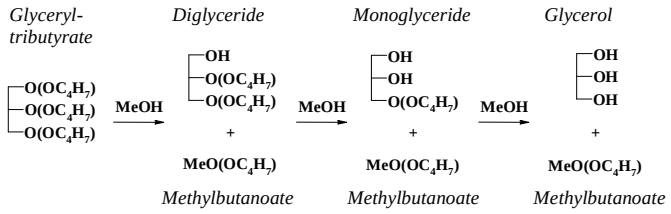


Scheme 1. Life cycle of fatty acid esters used for biodiesel.

Commercial biodiesel is produced from renewable resources including rapeseed, sunflower or soya bean oil which are composed of C_{14} – C_{20} fatty acid triglycerides. These are converted to the respective alkyl ester and glycerol by transesterification with short chain alcohols, typically methanol or ethanol. Transesterification can be performed using homogeneous basic catalysts, including Na or K hydroxides, carbonates or alkoxides. Base catalysis is preferred to acid catalysed routes using sulphuric or sulphonic acids, which are more corrosive with lower activities. However removal of the base after reaction is a major problem since aqueous quenching results in the formation of stable emulsions and saponification, making separation of the methyl ester difficult[3]. The use of a solid base catalyst offers several process advantages including the elimination of a quenching step (and associated basic water waste) to isolate the products, and the opportunity to operate in a continuous process[4,5] .

A variety of solid bases are known including alkali or alkali earth oxides, supported alkali metal ions, basic zeolites and clay minerals such as hydrotalcites.[6] Of the alkali earth oxides Ca-derived bases are the most promising as they are inexpensive, exhibit low methanol solubilities and are the least toxic. In addition promotion and control of basicity can be achieved via doping with alkali metals. Hydrotalcites ($[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]^{x+}(A_{x/n})^{n-}.yH_2O$) are another interesting class of solid base whose acid/base properties can be easily controlled by varying their composition[7]. The structure of hydrotalcites is based upon layered double hydroxides with brucite like ($Mg(OH)_2$) hydroxide layers containing octahedrally coordinated M^{2+} and M^{3+} cations. A^{n-} is the counter anion which resides in the interlayer space to balance the residual positive charge of the hydroxide layers which results from isomorphous substitution of M^{2+} by M^{3+}. Variation of the Al content, (x) can modify the basic properties of the material, with stable pure hydrotalcite structures reported to form for compositions over the range $0.25 < x < 0.44$.

Here we report on the characterisation of a series of Li-doped CaO[8] and Mg-Al hydrotalcite[9] catalysts and correlate their physicochemical properties with their activity in biodiesel synthesis using glyceryl tributyrate as a model substrate for screening catalytic activity (**scheme 2**).



Scheme 2. Transesterification of glyceryl tributyrate with methanol to glycerol and methyl butanoate.

Experimental

Catalyst Preparation. A series of $LiNO_3$ impregnated CaO catalysts were prepared by wet impregnation with Li loadings in the range 0.26 - 4 wt %. In a typical preparation 10 g of CaO (Aldrich 99.9 %) was impregnated using 50 cm^3 of an aqueous $LiNO_3$ (Aldrich 99.9 %) solution of appropriate concentration. The slurry was stirred for 2 hours, then dried at 100 °C for 24 hours.

Mg:Al hydrotalcites were synthesised using an alkali free route to minimise risk of catalyst contamination according to the following method. 50 cm^3 of distilled water was heated to 338 K under vigorous stirring. To this, 100 cm^3 of an aqueous mixture of x mol $Mg(NO_3)_2.6H_2O$ and y mol $Al(NO_3)_3.9H_2O$ was added slowly over a period of 1 hour along with 100 cm^3 of an aqueous solution of 0.2 mol $(NH_4)_2CO_3$. The Mg:Al ratio was varied such that x+y = 0.15 mol and x:y = 1:1, 2:1, 3:1 and 4:1. The pH of the mixture was continuously held at pH 7.6 - 8 by the dropwise addition of NH_4OH (as 35% aqueous ammonia solution). The resulting mixture was held at 338 K while stirred vigorously for 3 hours and then filtered and washed with distilled water until the filtrate was as near pH 7 as possible. The precipitate was dried in an oven at 373 - 398 K for approximately 18 hours. All materials were calcined at 723 K for 3 hours and cooled under a flowing stream of wet nitrogen (100 $mlmin^{-1}$, relative humidity 95%) before catalyst testing. Reference Al_2O_3 and MgO materials were synthesised by the same method.

Catalyst Characterisation and Screening. Bulk and surface properties of the resulting catalysts were determined by a combination of elemental analysis, DRIFT, XRD, SEM, XPS and N_2 porosimetry. Transesterification reactions were performed at 60 °C using 0.01 mol of glyceryl tributyrate (Aldrich 98 %), 11.87 g of methanol (Fisher 98 %) and 0.1 g of dihexyl ether (Aldrich 97 %) added as internal standard with off-line GC analysis. Unless stated otherwise, 0.1g of Li/CaO or 0.05g of hydrotalcite were employed.

Results and Discussion

Li doped CaO catalysts. The evolution of surface species formed on CaO following $LiNO_3$ impregnation was followed by XPS. A strong loading dependent variation in the Li electronic state is indicated from a progressive shift in the Li 1s binding energy from ~56.3 eV to 55.7 eV for the highest loading 2.4 and 4 wt% Li samples is observed, matching that of the $LiNO_3$ reference. The

variation in Li 1s binding energy with loading is shown in **figure 1**, together with the corresponding integrated Li 1s and N 1s intensities.

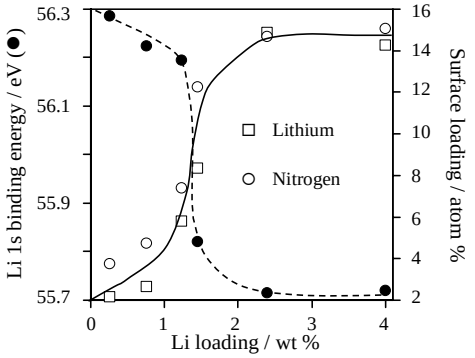


Figure 1. Correlation between Li 1s XPS binding energy and Li and N surface concentration as a function of $LiNO_3$ loading.

The transesterification of glyceryl tributyrate was subsequently investigated using this series of $LiNO_3$/CaO catalysts. A progressive conversion of the tri-glyceride to the methyl ester was observed, via first the di- and then mono-glycerides was observed as proposed in reaction scheme 2.

The initial rate of transesterification increased continuously with Li loading in the low surface coverage regime, passing through a maximum at 1.23 wt% Li. Higher loadings, associated with multilayer (bulk) $LiNO_3$, produced a dramatic decrease in activity. A strong correlation between the concentration of perturbed surface Li species identified in **figure 1** and the catalytic activity of Li-doped CaO is observed as shown in **figure 2** shows that both pass through a sharp maximum for 1.23 wt% Li and fall as bulk $LiNO_3$ overlayers are formed. Clearly the electronic state of Li in the submonolayer regime is critical to maintaining high activity in transesterification.

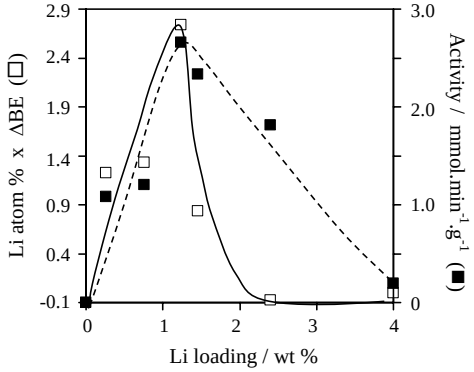


Figure 2. Correlation between activity and number of electronically perturbed Li sites in Li/CaO catalysts.

Mg/Al hydrotalcite catalysts. An alkali free precipitation route was successfully employed to prepare $[Mg_{(1-x)}Al_x(OH)_2]^{x+}(CO_3)_{x/n}^{2-}$ hydrotalcite materials with tunable basicity. The composition was varied over the range x = 0.25 – 0.55 with all resulting materials found to exhibit characteristic XRD patterns of the hydrotalcite phase. XPS revealed a decrease in both the Al and Mg photoelectron binding energies with Mg content which correlates precisely with the decrease in intralayer electron density resulting from exchange of Al^{3+} with Mg^{2+} in the brucite like layers. All hydrotalcite materials were effective catalysts for the transesterification of glyceryl tributyrate with methanol. The rate of tributyrate conversion and associated methyl butanoate and diglyceride formation were both first-order in triglyceride concentration. The initial rates for glyceryl tributyrate transesterification increased continuously with Mg content across the hydrotalcite series as shown in **figure 3**, while pure Al_2O_3 was completely inactive.

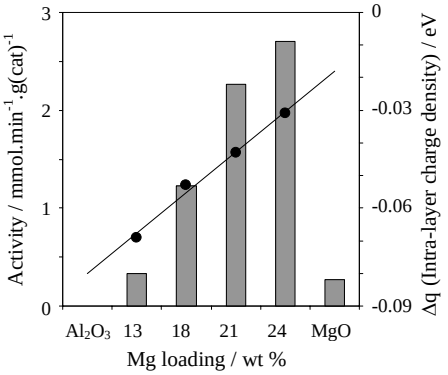


Figure 3. Initial rate of glyceryl tributyrate transesterification as a function of Mg content and change in intra-layer charge density for Mg:Al hydrotalcites.

The activities of the higher loaded 21 and 24 wt% Mg hydrotalcites are comparable to those reported for the best alternative Li-doped CaO solid base catalysts of 2.5 $mmol.min^{-1}.g(cat)^{-1}$. Pure MgO shows a lower activity and selectivity which may be attributed to a reduced number of accessible basic sites associated with its low porosity compared to the hydrotalcite materials. The catalytic activities of these hydrotalcites show a striking correlation with their corresponding intralayer charge densities towards tributyrate transesterification. This increased intralayer electron density of the Mg rich hydrotalcites would be expected to correlates with the Mg 2p binding energy which shifts from 49.9 to 49.5eV as interlayer electron density and corresponding basicity of these materials increases.

Conclusions

Both Li-doped CaO and Mg:Al hydrotalcite materials are effective solid base catalysts for the transesterification of triglycerides. Surface characterisation reveals that in both cases the electronic state of the surface species can be correlated with catalyst activity. In the case of Li-CaO the optimum activity is obtained upon deposition of a monolayer of Li, whereas with Mg:Al hydrotalcites, catalyst activity increases steadily with Mg content.

References

(1) Antolin, G; Tinaut, F.V; Briceño, Y; Castaño, V; Perez C; Ramirez, A.I. *Bioresource Tech*., **2002**, *83*, 111.
(2) Ma, F; Hanna, M. A., *Bioresource Tech*., **1999**, *70*, 1.
(3) Gryglewicz, S. *Bioresource Tech.*, **1999**, *70*, 249.
(4) Ono,Y; Baba, T. *Catalysis Today*, **1997**, *38*, 321.
(5) Clark J.H.; and Macquarrie, D.J. *Chem. Soc. Rev*., **1996**, *25*, 303.
(6) Tanabe, K; Misono, M; Ono Y; Hattori, H. *Stud. Surf. Sci. Catal*., **1989**, *51*.
(7) Cavani, F; Trifiro, F; Vaccari, A. *Catal. Today*, **1991**, *11*, 173.
(8) Watkins R.S; Lee. A.F; Wilson K. *Green Chemistry*, **2004**, *6*,335.
(9) Cantrell D.G; Gillie, L.J; Lee, A.F.; Wilson, K; *Applied Catalysis A*, **2005** *in press.*